QUALITY CONTROL PROGRAM FOR A GEOCHEMICAL LABORATORY, DEPARTMENT OF GEOLOGICAL SCIENCES, UNIVERSITY OF SASKATCHEWAN, CANADA

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ABSTRACT

The quality of analytical data produced by geochemical laboratories has become progressively more important as complex decisions concerning the impact of development on the environment Public concern regarding the impact of resource, industrial, and agricultural development is placing greater pressure on the government to protect the environment (Zhou, 2013). The quality of such data is squarely dependent on adherence to quality control programs, which provide guidelines from which high quality, trustworthy data can be generated.

A unique quality control program was developed and implemented at the NSERC-IRC Aqueous and Environmental Geochemistry Laboratory. This program: 1) accommodate samples from unique environments; 2) documents and maintains the high level of confidence in the data produced; 3) provides standard quality control protocols; and 4) ensures the continued training of staff. The evaluation of data produced during 2013 revealed the strengths and weaknesses of the laboratory methods through comparison with data quality objectives.

The data produced by the laboratory during 2013 was evaluated and quality confirmed. It was determined that the results produced met the high standards required by the data quality objectives, with a few minor exceptions. The quality objectives were based on the end use of the data and consideration regarding the complex nature of the water samples collected from diverse geologic media. There was increased variability of results near the method detection limit of selenium, cadmium, and arsenic, although they still meet to standards required for water quality investigations. Investigations into variabilities will include re-evaluation of detection limits, identification of the source of discrepancy between the methods, and possible matrix interference. Protocols will continue to be monitored and changes to methods made when objectives are not achieved or there are changes in laboratory staff, equipment, or the specific requirements of the studies the laboratory supports.

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This thesis is dedicated to the memory of Dr. Robert Kerrich.

“In my life I have found two things of priceless worth - learning and loving. Nothing else - not fame, not power, not achievement for its own sake - can possible have the same lasting value. For when your life is over, if you can say 'I have learned' and 'I have loved,' you will also be able to say 'I have been happy.”

— Arthur C. Clarke

TABLE OF CONTENTS

LIST OF TABLES

Table page

LIST OF FIGURES

Figure page

LIST OF ABBREVIATIONS

Abbreviation	Meaning
%D	Percent Difference
a	y-intercept
amu	Atomic Mass Unit
Ar	Argon
As	Arsenic
b	Slope
Ba	Barium
Bdup	Blind Duplicate
Be	Beryllium
Bi	Bismuth
Br	Bromine
C_A	Concentration Added to Sample
CAL	Calibration Standard
CB	Calibration Blank
CBE	Charge Balance Error
CCS	Calibration Control Standard
Ce	Cerium
Cl	Chloride
C_{LFM}	Concentration Measured in Laboratory Fortified Matrix Sample
Co	Cobalt
CO_3	Carbonate
COC	Chain of Custody
cps	Counts Per Second
CRM	Certified Reference Material
C_s	Concentration Measured in Sample
DI	Deionized
DOC	Dissolved Organic Carbon
DQO	Data Quality Objective
Dup	Duplicate
EPA	Environmental Protection Agency
F	Fluoride
Fe	Iron
FRB	Field Reagent Blank
Ge	Germanium
H	Hydrogen
He	Helium
HPLC	High Pressure Liquid Chromatography
I	Iodide
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICS	Ion Chromatography System
IEC	Inter-Element Correction
In	Indium
IRM	Internal Reference Material
IS	Internal Standard
k	Numerical factor chosen in relation to the level of confidence required.
K	Potassium
KED	Kinetic Energy Discrimination
Kr	Krypton
LDPE	Low-Density Polyethylene
LDR	Linear Dynamic Range
LFM	Laboratory Fortified Matrix
LOD	Limit of Detection
LOQ	Limit of Quantification
LRB	Laboratory Reagent Blank
m_a	Molality of an Anion Species
MB	Method Blank
m_c	Molality of a Cation Species
MDL	Method Detection Limit
Mg	Magnesium
MSDS	Material Safety Data Sheet
MU	Measured Uncertainty
n	Number of Values
N	Nitrogen
Na	Sodium
Nd	Neodymium
NO_2	Nitrite

NO_3	Nitrate
NSERC-IRC	Natural Sciences and Engineering Research Council of Canada - Industrial Research Chair
O	Oxygen
P	Phosphorus
Pb	Lead
PES	Polyethersulfone
PO_4	Phosphate
PVDF	Polyvinylidene fluoride
Q	Sum of Squared Residuals
QA	Quality Assurance
QAO	Quality Assurance Officer
QC	Quality Control
QCM	Quality Control Manual
QCP	Quality Control Program
QCS	Quality Control Standard
r	Correlation
R^2	Coefficient of Determination
RF	Radio Frequency Generator
Rh	Rhodium
r_i	Residual
RM	Reference Material
RSD	Relative Standard Deviation
S	Sulfur
Sc	Scandium
SD	Standard Deviation
Se	Selenium
SIC	Spectral Interference Check
Sm	Samarium
SO_4	Sulfate
SOP	Standard Operating Procedure
SRC	Saskatchewan Research Council
Tb	Terbium
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
U	Uranium
U of S	University of Saskatchewan
USGS	United States Geological Survey
x	Independent Variable
x_1	Value 1
x_2	Value 2
x_f	Found (or Measured) Value
x_i	A Value in a Population
x_m	Mean
x_t	True Value
Y	Yttrium
y	Dependent Variable
Z	Valence Charge
α	Level of significance

CHAPTER 1
INTRODUCTION

1.1 Background and Motivation

Quality assurance (QA) has become progressively more important in recent years as new and complex decisions are now being made that concern the environment. Public concern regarding the impact of resource, industrial, and agricultural development is placing greater pressure on the government to protect the environment (Zhou, 2013). Environmental data are required to inform these decisions, and increasingly more is being demanded of these data and the analytical laboratories that produce them (Fernández-Boy, Cabrera, & Moreno, 1998; Ibe & Kullenberg, 1995; Taverniers, De Loose, & Van Bockstaele, 2004a).

The key function of an analytical laboratory is to produce high quality, trustworthy data. Regardless of the field of study or the application, high quality data must meet two key criteria: reliability and utility. Both reliability and utility are therefore required for trustworthy interpretation of results. Reliable data are results that are comparable regardless of origin, describe the measurement uncertainty within quality requirements, and document the confidence in the measurements. The utility, or appropriateness, of a method and results describes the adequacy of the method to fulfill the requirements of a particular analytical purpose or application and indicates if the desired level of confidence in the data is being met (Mitchell, Brown, & Fuge, 2006; Taverniers et al., 2004a; Thompson, 1992). The production of data that meet these criteria is squarely dependent on the establishment of and adherence to a formal Quality Control Program (QCP). This QCP provides vital foundation guidelines from which meaningful and scientifically credible data can be generated (Ibe & Kullenberg, 1995; Ministry of Water Land and Air Protection, 2003; Olivares & Lopes, 2012; Sims & Wolf., 1995; Taverniers et al., 2004a).

Generally, a QCP outlines the practical courses of action followed to ensure the reliability of the data. Although all analysts understand and practice quality control (QC) to some extent based on their training, professional pride, and the importance of the particular project, sufficiently detailed QC may be neglected during routine analysis. Therefore, an established, routine, quality control program can ensure methods are consistent between analyses and operators within the laboratory (Environmental Monitoring and Support Laboratory, 1979)

A QCP was developed and implemented at the NSERC-IRC Aqueous and Environmental Geochemistry Laboratory to document uncertainty and ensure confidence in the data being produced. Through the development of a QCP, protocols were standardized for all studies conducted in the laboratory (Sims & Wolf., 1995). A Quality Control Manual (QCM) was drafted to document all resources, policies, and procedures that make up the QCP. There are several literature sources from government, journals, and other organizations that provide a wealth of information regarding quality control. For example the US Environmental Protection Agency, Government of British Columbia, US Geologic Survey, Trends in Analytical Chemistry, Marine Pollution Bulletin, Journal of Geochemical Exploration, and Applied Geochemistry, ASTM International and Eurachem. There are gaps in the literature with respect to low concentrations (near the detection limit), small sample volumes, and unique and complex matrices. Because these issues are not addressed in the literature and due to the unique nature of the projects supported by the laboratory, a unique QCM was crafted based on several literature sources. It was key that an understanding of the geochemistry of the samples be understood in order to properly select methods and data quality objectives.

The aqueous samples that were evaluated, and best represent the current work of the lab, were collected from a mine waste rock site and the surrounding natural (unimpacted) area. There were three different samples types evaluated. The first and most abundant, were the drain samples. These were collected directly from rocks drains either at the toe of the drain or from piezometers and had the highest total dissolved solids. The squeezed samples were collected by mechanically squeezing wet core samples from both the waste rock piles and the natural system. Wet core samples required a minimum of 10% gravimetric water content to supply sufficient pore water for water isotope, major cation, and trace metal analysis. Waste rock piles had complex mineralogy, including pyrite, coal, and clays which impacted the geochemistry of the aqueous samples and therefore the analytical results. These had intermediate TDS and had limited sample volumes requiring either dilution for ICP-OES or in most cases not enough sample for OES at all. Finally, samples were also obtained by aqueous leaching of dried core samples from the waste rock piles and natural system. Core samples that had less than 10% gravimetric water content were leached instead of squeezed. These had the lowest TDS due to the dilution associated with leaching, which was a 3 to 1 DI water to solid sample ratio. For the

purposes of this evaluation, leach values were not calculated back to pore water. Blind duplicate samples were generated from aqueous leaching as the process was carried out.

In the process of drafting the QCP, the appropriateness of each method and the difficulties associated with it were investigated. An appreciation for the nature of the sample and the end purpose of the results was also considered when selecting analytical procedures. Although this document was drafted for a specific laboratory, it is also of use for other geochemical laboratories performing similar analytical research. It should be remembered that QA is an ongoing process and the QCP should be reviewed periodically to ensure it is meeting the requirements of the laboratory and the project (Mitchell et al., 2006).

1.2 Foundation Principles

The QCP is based on five foundation principles that dictate the policies and procedures guiding the activities of laboratory personnel and the ultimate goals of the analytical laboratory. These principles are to: 1) ensure the safety of the staff through engineered controls, standard procedures, training, and promotion of safe work practices by management; 2) provide high quality, consistent, and cost-effective data; 3) ensure all laboratory practices are performed in an ethical manner; 4) participate in and contribute to investigations of the natural environment; and 5) endeavor to be a leader in innovation and method development (Maloney, Norton, & Survey, 2005).

1.3 Objectives

The development and implementation of a QCP for the NSERC-IRC Aqueous and Environmental Geochemistry Laboratory was undertaken to: (1) accommodate samples from novel environments and projects; (2) demonstrate and maintain a high level of confidence in the data produced by the laboratory; (3) standardize analytical procedures; and (4) ensure the advancement of staff expertise with time as well as transfer of knowledge during staff turn-over. The objectives of this thesis were to: (1) develop a QCP that includes standard procedures and QC protocols that provide a foundation for producing high quality results; (2) investigate and document the quality of the data produced by the laboratory in 2013; and (3) make recommendations that will optimize the continuing production of high quality and reliable data where appropriate. The quality of the data produced was investigated by evaluating data several quality control protocols. Statistical analyses of chemical concentrations of these standards were

used to calculate location, variability, and potential bias from sample handling and analysis. Data produced in 2013 consisted of aqueous samples collected from (1) rock drains; (2) mechanical squeezing of core samples; and (3) aqueous leaching of core samples. Analytes of interest were selected based on the needs of current projects.

1.4 Scope and Constraints

This study focuses specifically on the analytical demands of the current research projects supported by the laboratory. These analytical methods are constrained to inorganic constituents including major ions and trace metals in samples of geologic origin. Samples evaluated in this document were collected from a mine site by three methods: (1) direct sampling from rock drains; (2) mechanical squeezing of core samples; and (3) aqueous leaching of core samples. Samples were analyzed over the course of 2013. As method validation is a time-consuming process and methods were validated prior to this quality investigation, method validation results are not presented. QC results were selected to be representative and only elements relevant to current studies and/or elements that were determined by more than one method are presented.

1.5 Significance of Study

A fundamental requirement of a research project is reliable data. To empower researchers, policy-makers, and industry to make decisions based on accurate information, the demands on data are high. Interdisciplinary and interorganizational research has become increasingly important for answering environmental questions, and therefore the data produced by multiple laboratories must be true and comparable (Fernández-Boy et al., 1998; Ibe & Kullenberg, 1995). The alternative is incorrect or unreliable data that bring about a high risk for incorrect decisions that may lead to higher costs, health risks, or illegal practices (Taverniers et al., 2004a). To produce reliable data, the laboratories must adopt good field and laboratory procedures as part of a QCP.

The effort required to produce high quality geoanalytical data is not insignificant. Aqueous samples often consist of complex matrices that may hinder the accurate quantification of low concentration analytes (Becker & Dietze, 1998). The laboratory must overcome physical, chemical, and signal interferences from the matrix (Salomon, Jenne, & Hoenig, 2002; Varma, 1991) as well as analyte losses and contamination during sample handling and analysis (Batley, 1999; Hoenig, 2001), especially in non-ideal conditions such as remote mines sites.

While evaluating the quality of the data produced during 2013, areas in which data quality objectives (DQOs) were and were not being met were identified. The determination of these strengths and weaknesses improved the laboratory methods and, as a result, increased the quality of the data produced. Although the purpose of each laboratory may differ, many of these dimensions are universal and can be applied elsewhere.

1.6 Thesis Organization

Including this introductory chapter, this thesis consists of five Chapters and two Appendices, beginning with Chapter 2 is a literature review in which relevant background information is presented. Chapter 3 describes the management of the laboratory and the methodology for sample collection and handling, equipment management, sample analyses, data processing and reporting, and statistical methods. A summary of QC results is presented in Chapter 4 and conclusions and recommendations are reported in Chapter 5. Appendix A consists of figures and tables are in Appendix B.

CHAPTER 2
LITERATURE REVIEW

A research study dependent on chemical analysis first requires the development of an analytical strategy to be successful. This strategy is generally comprised of several steps (Hoenig, 2001):

1) The rigorous definition of the study objectives, including the selection of analytes of interest, the number of samples to be collected, and the time frame of the study.
2) The selection of appropriate analytical methods to meet the data requirements of the study objectives and control potential errors introduced during analytical procedures.
3) The selection and collection of meaningful samples related to the study and the preparation of these samples. This includes considerations for collecting representative samples as well as sampling handling procedures that will minimize sample contamination or analyte losses during collection, transportation, storage, and analysis.
4) The accurate determination of the analytes associated with the study. This includes the measurement of analytes and potential interferents, evaluation of control standards, and data processing and reporting.
5) The interpretation of analytical results as a function of the investigated problem.
6) Drawing relevant conclusions based on the data generated.

Steps 2–4 describe the activities the laboratory undertakes and are discussed below. Steps 1, 5, and 6 are in the domain of the researcher and are not considered to be within the scope of this thesis. That said, communication between the laboratory and the researcher is needed to outline data requirements.

2.1 Analytical Methodology

With respect to aqueous samples of geologic origin, the selection of appropriate methods and the actual execution of those methods are not trivial undertakings. These samples often have complex matrices with the concentration of constituents ranging over several orders of magnitude. It can be challenging to accurately determine low concentration analytes with physical, chemical, and signal interferences from other constituents with high concentrations. The requirements of the method(s) that must be addressed include definition of analytes of interest, method detection limits (MDLs), precision, bias, sample throughput, cost, and

versatility. These categories form the DQO the laboratory must meet to satisfy the projects and studies it supports.

The Aqueous Geochemistry Laboratory produces analytical data on the chemical composition of rocks, sediments, and the fluids they interact with to better understand geological and geochemical processes. A major advantage of the congruent use of inductively-coupled plasma mass spectrometry (ICP-MS) as well as inductively-coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography (IC) is the ability to compare results that fall into overlapping concentration ranges, and therefore add confidence to the quality of data generated by each method. Much of this research has a focus on trace metals in groundwater, surface waters, and wastewater. The goals of these studies require low MDLs, even in complex matrices, and the simultaneous analysis of more than 60 elements. These requirements must be accomplished without compromising high precision or rapid throughput of samples. As a result, and with the guidance of EPA Method 6020A (Test Methods for Evaluating Solid Waste, 2007), a full suite of elements including trace metals and major cations are analyzed by ICP-MS. Major cation analysis must be versatile in complex matrices (simultaneously measuring several analytes over several orders of magnitude of concentration at various total dissolved solid (TDS) levels) without compromising rapid throughput. In addition, cost-effectiveness of the method is also desired. To fulfill these requirements, and with the guidance of EPA Method 200.7 (Martin, T.D., Brockhoff, C.A., Creed, 1994), major cations as well as select trace metals are analyzed by ICP-OES. Major anion analysis must also be versatile in complex matrices (simultaneously measuring several analytes over two to three orders of magnitude of concentration at various TDS levels). The cost-effectiveness of the method is also desired. As a result, and with the guidance of EPA Method 300.1 (Hautman, 1997), major anions are analyzed by IC.

2.1.1 Inductively Couple Plasma Mass Spectrometry (ICP-MS)

Inductively couple plasma mass spectrometry is a widely used technique for the sensitive determination of trace and ultratrace elements in all fields of modern science and technology. It is particularly well suited to aqueous environmental samples due to its rapid, multielemental capabilities in a variety of matrices (Salomon et al., 2002). Inorganic mass spectrometric methods are well established over a wide range of elements and concentrations, which allows for the determination of concentrations and isotopic abundances of major, minor, and trace constituents down to the ultratrace level (Becker & Dietze, 1998).

The basic principle of ICP-MS is relatively simple. The chemical constituents of the aqueous sample are decomposed into their atomic constituents and ionized in inductively coupled argon plasma (Becker & Dietze, 1998). Ionization is typically > 90% for most chemical elements and a low fraction of multiply charged ions (~ 1%) is produced. Positively charged ions are rejected from the ICP by the interface to the high vacuum of the mass spectrometer. Ions then proceed to the mass analyzer of the mass spectrometer where ions are separated according to their mass-to-charge ratio (and energy-to-charge ratio in the case of double-focusing section field ICP-MS) and detected by a photomultiplier. Although the basic principle is relatively simple, the ability to modify the system and technological advances continue to increase the utility of ICP-MS methods (Becker & Dietze, 1998).

ICP-MS is a routinely used technique due to several advantages of the system. First, the simple sample introduction system (nebulizer, spray chamber, and ICP) allows the possibility of coupling techniques to the ICP-MS (ultrasonic nebulization, flow inject high performance liquid chromatography (HPLC), hydride generation, electrothermal vaporization, laser ablation), which further increases its utility. Second, the temperatures of 5000–8000 K produced by the ICP result in the near complete evaporation of aqueous samples and the dissociation of sample molecules (Becker & Dietze, 1998). This decreases or eliminates chemical interferences by breaking chemical bonds. The plasma is also essentially oxygen free (Varma, 1991). Additionally, the high efficiency of ion production results in excellent detection limits. Technological advances such as low pressure helium (He) ICP-MS in combination with an ultrasonic nebulizer improves the utility of the ICP-MS by reducing ion intensities due to solvent loading. A collision cell for the reduction of energy spread (and therefore reduction of interfering molecules) has also improved the detection limits of routine ICP-MS analysis (Becker & Dietze, 1998). Although ICP-MS is a widely used technique as a result of these advantages, there are still limiting factors to its application(Salomon et al., 2002). The major potential problems encountered during routine ICP-MS analysis include ionization interferences, drift, variable matrices, and mass interferences (Salomon et al., 2002). Some matrix effects are specific to the method used while others affect ICP-MS, ICP-OES, and IC systems. General challenges with complex matrices are discussed in detail in Section 2.2.2 and variable matrix effects particular to ICP are presented here.

Drift, or overall instrument stability, is a potential source of error encountered during routine ICP-MS or ICP-OES analysis. This is especially challenging during large, unattended batches. Drift is a product of various subsystems including electronics, the nebulization system, frequency devices, variable intensity of the primary source, and increasing salt and carbon build-up on interface cones. For ICP analyses, periodic recalibrations are often performed during long, unattended batch runs to compensate for possible drift in operational conditions. Drift may be progressive (or non-existent) and occur between calibration blocks. In this case, the software can recalibrate and efficiently take into account the drift occurring over the entire series of samples that are analyzed between calibration blocks. Drift may also appear suddenly during the analysis period (non-linear drift). In this case, the software correction fails because the time and duration of the change is unknown. Fortunately, this type of drift is often detected and corrected if an internal standard (IS) is in use. Without an IS, non-linear drift may lead to erroneous values as a result of under- or over-estimation of the actual drift. In some cases, low concentration standards or samples may be reported as negative values if the correction leads to under-estimation of concentration values. Commonly employed internal standards include scandium (Sc), yttrium (Y), and indium (In), with In being the most popular choice as Y and Sc are more likely present in environmental samples (Salomon et al., 2002).

The variable concentration of acid in solutions may also produce variable matrix effects. ICP solutions are typically acidified with 2% nitric acid and an unknown amount of acid is consumed during this acidification. Hoenig (2001) tested the effect of increasing nitric acid concentrations (between 0.1–5%) on the determination of trace element concentrations. Fortunately, under standard ICP-MS conditions, the matrix effects due to variable acid concentrations were not significant and are not likely to be a major source of potential error (Hoenig, 2001).

Analytes with relatively high ionization potentials can also be a challenge in ICP. High ionization potentials result in a lower degree of ionization. Analytes such as phosphorus (P), arsenic (As), and selenium (Se) may only ionize 30–80% under standard operating conditions resulting in a reduced analyte signal (Hill, 2007).

The most important challenge to ICP-MS analysis is mass interference. These interferences are a major potential source of error in ICP-MS analysis (Becker & Dietze, 1998; Salomon et al., 2002). Mass interferences are produced by the high plasma temperature at high

gas pressure (1000 mbar). These conditions result in a multiplicity of plasma chemical reactions. These reactions lead to the formation of molecular ions with high ion intensities that may interfere with quantification of analytes of interest. Fortunately, the main interference problems have now been discovered and documented, and can often be overcome (Salomon et al., 2002). A common interference during ICP-MS analysis is an isobaric interference with As. Chloride (Cl) in the sample combines with argon from the plasma to form $^{40}Ar^{35}Cl^{+}$, which has an identical mass to ^{75}As. Because both masses are detected simultaneously, an apparently high concentration of As is reported (Hoenig, 2001). Therefore, the use of hydrochloric acid is typically undesirable in ICP-MS analysis because it contributes Cl to the matrix. Another common challenge is the determination of Se concentrations in the presence of a 82-Krypton (^{82}Kr) isobaric interference with ^{82}Se (Salomon et al., 2002). Usually, the ICP-MS software will include the possibility of introducing equations that allow for the correction of interfering species for a selected isotope. The most well-known equations concern the correction of ^{75}As for $^{40}Ar^{35}Cl^{+}$ and ^{82}Se for ^{82}Kr interference. The basic concept behind these corrections is simple; it is based on the ratio between the natural abundance of the interfering constituents. For example, the ratio of $^{82}Kr/^{83}Kr$ can be used to correct for any addition of ^{82}Kr to the ^{82}Se signal. These correction equations are usually introduced into the software by the manufacturer (Hoenig, 2001).

The use of correction equations is not always straightforward. Salomon et al. (2002) observed that the ^{83}Kr signal was higher than the ^{82}Kr signal when they should have been of equal intensity. Although the reason for this observation is unknown, the resultant correction equation then leads to a systematically strong overcorrection for Se concentrations. This overcorrection, especially at the low end of the Se calibration curve, will result in negative concentrations being reported. Therefore, many laboratories do not always use the Kr correction equation, and instead rely on blank procedures to correct for Kr interference (Salomon et al., 2002). Matrix interferences can also be managed by the addition of small volumes of standard to the analyte solution (standard addition). The use of separate calibration standards that are not matrix-matched can be a significant source of error (Batley, 1999).

2.1.2 Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES)

With respect to the analysis of major, minor, and trace constituents, ICP-OES has been one of the choice methods since the 1930s. Advances in technology have allowed the system to deal with virtually all types of samples. After the commercial development of improved ICP in the 1980s, ICP-OES has become one of the most advanced chemical analysis techniques. The ability to determine elements at concentrations over orders of magnitude, especially low concentrations, makes ICP-OES a powerful tool in the analytical laboratory that is able to deliver sensitivity, precision, speed, accuracy, and convenience (Varma, 1991). Disadvantages of OES include spectral interference and signal suppression (Hoenig, 2001; Varma, 1991).

The ICP source coupled to an OES utilizes the same technology as an ICP-MS. The ICP technique, and its advantages and disadvantages, are discussed in detail above (Section 2.1.1). After the sample passes through the plasma, the elements present in the sample are desolvated, dissociated, atomized, and excited. This excitation results in the emission of light of unique frequencies for elements (Varma, 1991).

Spectral or background interference in ICP-OES are produced when the background shifts due to light emission at the same wavelength as the analyte of interest and causes interference. Three types of spectral interference may result from the matrix, solvent, air, or gases: stray light, partial overlap of nearby or wing-broadened spectral lines, and direct overlap of unresolved spectral lines. These interferences can be overcome with proper wavelength selection, background corrections, interfering element correction (IEC), and software corrections using an IS (Varma, 1991).

Signal suppression due to the use of acids is a possible source of error during ICP-OES analysis. Nitric acid is usually the most desirable reagent because, although signal suppression occurs, no severe analytical problems are practically observed at concentrations up to 10% (or sometimes higher) if concentrations are similar in standards and samples (Hoenig, 2001).

2.1.3 Ion Chromatography (IC)

Ion chromatography is a widely accepted and recommended analytical technique for successful determination of ions in diverse types of environmental samples (Fernández-Boy et al., 1998). Soon after its introduction in 1975, IC was applied to various fields and matrices. IC has been advancing to the point that it is the routine analytical method and the workhorse of analytical determinations of anions (Sedyohutomo, Lim, & Takeuchi, 2008; Singh, Abbas, &

Smesko, 1996). The suppressor technology was a key advance in IC techniques that greatly reduces the background conductivity of the eluent and also increases the analyte signal, resulting in widespread use of the technique (Sedyohutomo et al., 2008). The determination of major anions, including fluoride (F^-), Cl^-, bromide (Br^-), iodide (I^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), and oxalate in environmental waters is the dominant area where suppressed IC has replaced the use of separate analytical methods (Fernández-Boy et al., 1998).

Prior to the widespread use of IC, inorganic anions in drainage and soil solutions were typically analyzed by separate analytical methods, many of which are time consuming, laborious, and require specific analytical skills. As a result, IC has become a popular alternative with the advantages of speed, simple operation, and easily obtained results as well as versatility and high sensitivity. This technique can separate ionic species into discreet bands in a liquid mobile phase using a variety of separation modes and detection technologies. Also, it is relatively inexpensive to operate and in many cases the sample preparation required is minimal (Fernández-Boy et al., 1998). The determination of major anions in environmental water samples that are generally analyzed by an IC system (ICS) can be made with good reliability. In most environmental waters, the concentrations of anions are within an order of magnitude of each other, which allows for their simultaneous determination. Also, the pretreatment of samples for inorganic anion analysis by common IC techniques generally only involves simple steps such as filtration, sample dilution, pH adjustment, protein precipitation, and/or extraction of the analyte. In fact, the determination of anion by suppressed IC is so common that the reliability is often taken for granted (Singh et al., 1996). However, there are cases in which potential errors may be introduced, including changes in baseline, matrix effects, and high TDS.

Changes in baseline conductivity will affect the quantification of analyte anions due to an increase in the signal to noise ratio. The baseline may be affected by changes in analyte pH and variations in eluent concentration. The preparation of off-line eluent may introduce error because fluctuations in eluent concentration greatly impact both the baseline and the separation of analytes (Singh et al., 1996). Therefore, an electrochemical process called electro-elution has been introduced as a way of generating or moderating the mobile phase. The major advantage of this process is the precise control of the eluent concentration by control of the electrical current flowing through the eluent generation device. As a result, water is the only reagent required for

eluent generation and both gradient and isocratic elution can be precisely and consistently generated (López-Ruiz, 2000).

Potential errors may be introduced during more complex IC techniques that require more sample pretreatment or more careful analysis. These errors often arise when the concentration of all constituents in samples are very low (e.g., rainwater), when the matrix constituents are relatively high compared to the analyte of interest, or when the matrix constituents are a source of interference in the IC separation. Erroneous results in anion quantification are often produced when determining small or trace concentration of anions in the presence of large concentrations of matrix ions. This error may be due to the incomplete resolution of analyte peaks from the baseline and/or overloading of the analytical column by matrix ions. Error introduced as a result of column overloading occurs when matrix anions occupy all or most of the exchange sites on the column. This results in peak broadening or asymmetry in the peak of the anion of interest (López-Ruiz, 2000).

Other quantification difficulties may occur when certain anions (including SO_4) are underestimated as a result of high concentrations of salts. Some anions may be unaffected (Cl, Br, and I) as long as the baseline resolution is obtained. This is not thought to be the effect of the large concentrations of other anions, but rather of the corresponding cation (Na). The suppressor exchanges the influent cations for hydrogen ions and therefore reduces the eluent conductivity and converts common anions such as Cl, Br, I, and SO_4 into strongly ionized acids (HCl, HBr, HI, H_2SO_4, respectively). Complete and fast exchange of the anions is required but, when influent cation concentrations suddenly increase, a significant accumulation of hydrogen ions occurs on the surface of the suppressor. This accumulation results in the formation of HSO_4 ions, which has a lower conductivity than H_2SO_4. The proton-anion association may also result in the broadening of the SO_4 peak. This is only relevant for anions that are capable of forming strong ion pairs with protons. Anions of strong acids such as Cl, Br, and I are not affected by this interaction and their concentrations should be accurately determined by suppressed IC in water samples with high salt matrices as long as the column is not overloaded. When analyzing new types of samples, it is recommended that several analyses be done at different dilutions until a stable measurement is made to determine if there are any matrix effects (Singh et al., 1996).

2.2 Common Analytical Challenges

The accuracy of results produced by an analytical laboratory is influenced by numerous steps beginning with sample collection, continuing through sample preparation, and ending with the determination itself (Hoenig, 2001). The sample handling strategy involves field sampling, chemical analyses, data reporting, and all QA/QC procedures associated with each step (Batley, 1999). It is often the case that the available sample volume restricts the possible measurement of properties. Therefore, it is vital that a study design plan consider which analyses are best suited to meet the objectives of the research based on both the desired information and the volume required for each analysis. In these cases, the most important variable(s) of the system (those of the greatest interest) should be selected in consideration of knowledge from the published literature. Some properties must also be immediately measured during field sampling because sample conditions can change quickly and compromise the sample. Conditions such temperature, suspended matter, pH, redox, and surface tension should either be quantified in the field or accounted for during the selection of sample containers, storage, and transportation (Paschke, 2003).

Temperature can affect solubility and stability of analytes as well as other physicochemical properties (pH, redox, surface tension) and, therefore, should be taken into account during transport and storage (Batley, 1999; Hoenig, 2001; Paschke, 2003). It is recommended that samples be kept at a low temperature (4 °C) until just before analysis (Paschke, 2003). There is some debate over the practice of freezing samples to inhibit chemical and bacterial reactions (Hoenig, 2001), as freezing may result in either selective concentration of analytes and/or possible losses during thawing (Batley, 1999).

Suspended matter or colloidal inorganic and/or organic substances cause turbidity in water by scattering the light on its way through the sample (Paschke, 2003). Silica particles (clay), ferric/aluminum hydroxides, organic macromolecules (humus), and microorganisms may all cause such effects. These materials can undergo changes during sample transportation and storage and act as sinks or sources of analytes, thus drastically influencing analytical results. Surface tension of water is very sensitive to impurities and most organic substances reduce the surface tension of water considerably. Even a relatively small change in surface tension can indicate the possible presence of colloids (micelles) that may affect analyte concentrations and could necessitate the use of a microemulsion-breaking agent before continuing with sample

preparation. Other various organic compounds are ubiquitous in natural waters which may influence results are the degradation products of plant and animal tissue, humic substances, residues from coal and oil processing and fuel combustion, detergents, pesticides, and so on. The presence of total organic carbon (TOC) and dissolved organic carbon (DOC) also controls the mobility and distribution of trace-metal ions by acting as a sink or source. This control can strongly influence analytical sample preparation as well as calibration by producing matrix effects (Paschke, 2003).

One of the most important and influential parameters in water chemistry is pH. It influences stability, reactivity, and mobility of constituents including elements as well inorganic and polar organic compounds in environmental systems. Reduction and oxidation (redox) reactions also greatly influence the behavior of constituents in most environmental systems (Paschke, 2003). Together with pH, redox affects the concentration of dissolved chemical species. The redox potential (Eh) represents all corresponding redox pairs contained in solution after chemical equilibrium is established. Eh values that are positive (in mV) indicate aerobic (or oxic) conditions and Eh values below -200 mV indicate strict anaerobic (anoxic) conditions. It is challenging to maintain the Eh conditions of a water sample after collection using reducing or oxidizing agents without compromising sample integrity. Therefore, meaningful determinations of Eh in environmental samples should be done immediately (Paschke, 2003).

2.2.1 Sample Handling

Correct interpretation of results depends heavily on the quality of the samples analyzed. The common computer science phrase “garbage in, garbage out” applies well to the collection and preparation of samples before analysis. In other words, “[d]oes it make sense to apply a highly accurate (and expensive) analytical procedure to samples for which the results are partly erroneous from the outset because of incorrect sample collection and storage?” (Paschke, 2003).

As part of an environmental study, samples are first collected and then analyzed to gain information on the concentration and stability of elements and compounds in natural processes and materials. Fundamental thermodynamic, kinetic, and electrochemical conditions characterize the reactions and transport processes that occur, which vary greatly in time and space. Therefore, the “exact values” determined or mean/median values of concentrations of constituents are useable only if variation in critical properties of the matrices is taken into account. Sample preparation is intended to transfer or transform the analytes of interest into measureable forms.

As a result, it is almost inevitable that the interactions of elements and compounds will be changed as a result of changes in the chemical environment. These interactions are a function of the physical and chemical properties of all constituents of the sample. This affects the applicability of different sample preparation techniques and analytical methods as well as their efficiency and reproducibility. Therefore, the characterization of the initial physicochemical state of the sample is important in the selection of all further sample collection and preparations steps (Paschke, 2003).

Sample handling can be divided into two steps, sample collection and sample preparation, both of which greatly influence the quality of the data produced and subsequent interpretations. Two common types of error can result from poor sample handling: analyte losses or analyte contamination (Hoenig, 2001). Analyte loss or contamination has become a greater potential source of error in recent years concurrent with the dramatic lowering of detection limits; many of these type of errors were practically imperceptible when previously determining high concentrations of analytes with less sensitive techniques (Batley, 1999; Hoenig, 2001).

The proper selection of sample collection procedures can mediate potential errors before the sample even reaches the laboratory for analysis. Sampling is the first and one of the most important steps in almost any research study. The sampling tools, filtration devices, and storage vessels are all sources of potential error and must be carefully chosen and cleaned to minimize this risk. During sample collection, risks of analyte losses or contamination can become critical when they concern sampling of a media that has very low concentrations of analytes of interest (Hoenig, 2001). To select appropriate sample collection procedures, the potential errors and their impact on the goals of the research study should be understood.

The first major potential error with respect to sample collection is analyte losses. Analyte losses, or incomplete recovery, may be the result of volatilization, absorption, transformation, precipitation, or coprecipitation caused by the treatments used during sample collection, preparation, and analysis (Hoenig, 2001). Analyte losses are generally the product of adsorption of metal ions onto the vessel or the suspended particles. Contamination and/or absorptive losses generally result from improper sample container selection, inadequate container preparation, effects of sampling devices, sample preservation, and/or storage (Batley, 1999). Aqueous solutions are typically acidified with nitric acid immediately after sampling to a pH < 1.5 (Hoenig, 2001). This acidification is generally sufficient to prevent adsorption onto the walls of

the vessel for relatively long time periods. It should be noted that it can be very difficult to remobilize previously absorbed trace elements back into solution. Acidification of samples may also mobilize some trace elements associated with particulate matter in the sample. This may be problematic if only the trace content of the aqueous phase is to be determined, in which case the sample should be filtered (typically using a 0.45 μm membrane filter) and subsequently acidified. If the total content of trace elements in the water sample is to be measured, the dissolution of suspended matter is desirable. There can also be apparent losses even in cases without any true loss due to possible interferences that may be responsible for analyte signal suppression. This apparent loss is attributed to sample matrix effects, resulting from differences in composition of the calibration standards and samples. In these cases, the measurement technique is responsible for the observed error (Hoenig, 2001).

The second major potential error associated with sample collection is contamination. Contamination, or excessive recovery, is the result of systematic or random introduction of non-negligible amounts of analyte during sample collection, preparation, and analysis. Contamination from reagents, other materials utilized, or from ambient air is generally reproducible between samples, and the error is systematic. It is therefore important to use ICP-MS grade reagents for ICP-MS and ICP-OES analyses. Possible global contamination can be recognized and accounted for by evaluating several representative blanks and considering them in the calculation of results. Random error from other contamination sources is more easily avoided. It is of importance to distinguish the type(s) of error in effect, determine the source(s), and manage accordingly (Hoenig, 2001).

To determine the extent of contamination or analyte losses and mitigate the effects, sampling QA should include field blanks, container blanks, and trip blanks. A field blank is a sample container filled with laboratory reagent blank (LRB) water that is taken out to the field and subjected to all of the same processes as the sample containers (Batley, 1999; Bosnak, 2007; Hautman, 1997; Martin, T.D., Brockhoff, C.A., Creed, 1994). This includes transportation to and from the field, opening in the field environment, filtering, preservation, and storage. A container blank only measures the effects of the sample container on the LRB and the trip blank only measures the effects of transportation. Generally, only a field blank is required unless error is high, in which case the other blanks will help identify its source. A field fortified sample can also be used to measure analyte losses during transportation and storage; a sample container with

LRB water is spiked with analytes of interest and recovery calculated. Finally, sample replication can reveal information regarding the magnitude of sample and analytical variability (Batley, 1999).

The conditions under which samples are stored can greatly influence analytical results. The effects of adsorption can be minimized by storing samples in a refrigerator (in the dark) at 4 °C. Storage at higher temperatures and exposure to light can lead to enhanced bacterial growth in the sample and on the container walls, which can be a possible sink for metals or a source of interference (Batley, 1999; Hoenig, 2001). Acidification of samples will inhibit growth, but should only be done after filtration (Batley, 1999). The practice of freezing samples is debated as it can inhibit chemical and bacterial reactions over longer periods of time (Hoenig, 2001); freezing may also cause selective concentration of analytes and/or analyte losses during thawing (Batley, 1999).

Sample preparation is the manipulation of a sample before it can be presented for instrument analysis. For water samples, this typically only includes filtration. In some cases, sample preparation includes several steps and the procedures associated with those steps are of the highest importance when ensuring good quality data, especially with respect to trace analysis. Contamination or analyte loss risks increase with temperature, pressure, the use of several reagents, and contact with vessels. Risk control protocols are based on a number of key principles that must be fulfilled to minimize contamination and/or analyte losses during sample preparation. Batley (1999) and Hoenig (2001) recommend:

1) Reviewing and adhering to established procedures as well as understanding the objectives of the study.
2) Ensuring a clean laboratory environment.
3) Limiting the mass of the sample to be prepared and analyzed as well as the volume of the vessels used. Vessels may be of porcelain, glass, quartz, polytetrafluoroethylene (PTFE), platinum, or various plastics. These materials may affect analyte loss due to adsorption or contamination, particularly if they are in contact with samples and standards for long periods of time.
4) Using either high grade water and chemicals or purifying reagents in the laboratory. Reagent impurity produces a key and often systematic source of contaminants.

5) Ensuring all vessels are clean by soaking in acids followed by abundant rinsing with deionized water.
6) Avoiding old, worn, or scratched vessels to avoid adsorption of trace elements to damaged surfaces.
7) Simplifying handling and avoiding filtration or transfers of solutions unless necessary. If filtration is necessary, ensure the filtration equipment is clean. The filtration of a LRB and several successive aliquots of sample is recommended to determine the extent of contamination and/or losses.
8) Preparing blank solutions using the same reagents, vessels, and operating conditions as samples and standards to evaluate potential contamination or analyte losses and, in some cases, correct the results.
9) Checking the recovery of analytes using reference materials of composition similar to samples.

2.2.2 Complex Matrices

The complex nature of many matrices is a major potential source of error for many types of analytical measurements. Although the nature of the matrix may cause difficulties depending on the method chosen (for example, mass interferences in the case of ICP-MS), some matrix characteristics pose difficulties for several analytical methods. The matrix can be responsible for additional difficulties encountered during analyses because it constrains the preparation steps required, the efficiency and mode of analyte introduction, and signal determination; it may also be a source of cross-contamination. The degree of difficulty with respect to dealing with the matrix is usually a function of matrix complexity and/or concentration levels as well as the analytical technique used (Hoenig, 2001).

In ICP-MS and ICP-OES analyses, several well-known difficulties are associated with the complexity and concentration of the sample matrix, including viscosity, surface tension, and solids content (Varma, 1991). Variations in the viscosity of the standards and samples are a concern when a nebulization system is used for solution introduction. The physical differences due to viscosity variations result in changes in the formation and/or transportation of the aerosol produced in the nebulizer (Hoenig, 2001; Varma, 1991). The utilization of sulphuric acid is often avoided for this reason. Unless the concentration of sulfuric acid is identical in all solutions analyzed (standards and samples), the variations in aerosols can be a potential source of error. It

is often challenging to ensure all solutions have the same concentration of sulfuric acid because the true amount of acid consumed during mineralization and acidification remains unknown. For this reason, the use of sulphuric acid is often avoided (Hoenig, 2001). The presence of organic matter and salt content are also a potential challenge during ICP analysis. These may cause spectroscopic interferences, build-up on the interface cones (Salomon et al., 2002), and overloading of the plasma (Hoenig, 2001). To avoid matrix deposition and minimize the matrix effects, the upper limit of solid content tolerated by ICP-MS is generally less than 0.2% (Hoenig, 2001) or 0.5% (Varma, 1991). Therefore, appropriate dilution of samples is more important with ICP-MS than with other techniques, such as ICP-OES, that are able to deal more effectively with the increased presence of matrix constituents (Hoenig, 2001). Fortunately, the low detection limits achieved by ICP-MS ensure the determination of analytes at low concentrations. Overloading the plasma may also cause long-term stability issues in the system as the matrix may obstruct cones, enter the vacuum system, and deposit on the ion lens components (Hoenig, 2001).

2.3 Quality Assurance and Quality Control

Analytical methods are complex, multi-step processes that begin with sample collection and end with the final generation of a result. Every method has a specific scope, application, and analytical requirement. Regardless of these differences, the basic principles of QA are the same (Taverniers, De Loose, & Van Bockstaele, 2004b).

QA is the complete organizational infrastructure that forms the foundation for all reliable analytical measurements (Batley, 1999; Simonet, 2005; Taverniers et al., 2004b). It is the system of procedures designed to ensure results meet DQOs. It includes the overall management of project planning, sampling, documentation, staff training, consistency in handling samples, analyses, validation, and reporting. QA protocols document the performance of all aspects of the laboratory work by measuring against defined standards to verify that desired DQOs are being met (Batley, 1999; Ministry of Water Land and Air Protection, 2003; Taverniers et al., 2004b). Data based on inadequate QA can be in error and their misuse can lead to a variety of issues including financial, environmental, and legal consequences (Batley, 1999). Although the use of QA does not eliminate the potential errors and guarantee accuracy, it can control the quality of the data and ensure that the DQOs are being met and define the degree of fulfillment of expectations. To control the quality of data, the parameters that denote the quality of a certain

chemical analysis must be defined and fixed. QA can be divided into QC and quality assessment (Simonet, 2005; Winter, Budde, Novielli, & Costle, 1993).

The objectives of QC protocols are to provide precise, accurate, reliable, and cost-effective sampling techniques, analytical methods, and data reporting procedures. These technical protocols and laboratory practices are specifically undertaken to reduce errors all the way from sample collection to final sample reporting and define what remedial action must be taken if errors are discovered (Ministry of Water Land and Air Protection, 2003). QC protocols outline DQOs, which are the qualitative and quantitative statements of the levels of acceptable uncertainty in the results. DQOs provide the statistical basis for planning investigations and generating data that meets the user's needs. With proper evaluation (assessment), the measured data over time can be used to determine whether these needs are being met and to flag potential problems (Winter et al., 1993).

The objectives of the assessment program are to provide continuous review and evaluation of the data being generated to ensure that the QCP is being implemented properly and functioning according to DQOs (Winter et al., 1993). In other words, quality assessment is comprised of processes used to monitor and document the effectiveness of the QC protocols. These processes will document both accuracy and precision. Accuracy is how close a measurement is to the known value and precision is the agreement of multiple measurements of the same sample. Together, accuracy and precision offer a characterization of analytical uncertainty in the data (Sims & Wolf., 1995). Adherence to the guidelines ensures that problems are identified and remedied when encountered (Ministry of Water Land and Air Protection, 2003).

2.3.1 Quality Control Protocols

To achieve DQOs, a QCP introduces a set of activities and techniques that monitor the performance of the laboratory. Because method validation is time-consuming, certain relevant tests using quality control solutions can be routinely carried out after validation is complete to ensure the instrument is still working properly. In general, a minimum of 10% of samples should be control and calibration standards. These standards should produce results within an agreed percentage of a certain value, which will be a factor of the concentration being measured. Lower precision for ultratrace concentrations is expected compared to trace concentrations or above

(Batley, 1999). Quality control solutions include reference materials, QC standards, calibration control standards, and blanks.

Reference materials (RMs) are one of the most well used tools to evaluate accuracy of an analytical process. RMs can either be purchased certified RMs (CRMs) or internal RMs (IRMs) with known values that are analyzed with each batch of samples. IRMs are typically large amounts of a material that are stable with time and contain analytes of interest and possible interferences. Samples can also be fortified (laboratory fortified matrix, LFM) with analytes of interest and prepared with possible interferents. By analyzing a sample and the associated LFM, recovery can be calculated and the extraction efficiency of a method can be determined. Records of results are kept and used to evaluate the quality performance of the method. Deviations from acceptable limits notify the analyst immediately and lead to rapid changes in procedure to remedy the issue (Masson, 2007). CRMs can be used in bias studies to demonstrate that a method is not significantly biased as well as in precision and robustness studies to evaluate the effects of variability of conditions, operators, equipment, and time (Taverniers et al., 2004a).

Quality control samples or standards are monitored to check the calibration or evaluate the performance of methods, instruments, or analysis (Winter et al., 1993). Control samples are a vital tool in ensuring the accuracy of an analytical method. Control samples, with known concentrations, are treated the same way as routine samples and the accuracy of the method can be used by comparing the known value to the experimental value. It is important that the control sample has the same concentration range as typical samples, is homogenous, and is stable with time. An inappropriate control standard will offer no indication if the method is meeting the requirements. Control standards used to verify the calibration are called calibration control standards (CCSs). Although, there is no general rule describing the number of control samples included, it is recommended that 10% of samples should be dedicated to QC (QC samples, duplicates (Dup), CCS, LFM). Randomizing the position of the control samples is recommended, and control samples should follow immediately after calibration to check that the calibration is valid and the entire system is working correctly. It is also of interest to note other parameters. In IC analysis, for example, such parameters would include peak shape, retention time, gradient performance, and sensibility (peak area/height). The retention time of a peak during separation is often a useful tool to identify problems with the system (temperature, impurities, back pressure)

and with a separation (mobile phase composition, column degradation), although small variations are normal (±0.1 min) (Masson, 2007).

Blank samples are another useful tool to monitor the performance of a method, and are treated similar to control samples. These samples are included in each analytical batch and follow the same sample preparation as the unknown samples. This includes such steps as filtration, transportation, and storage as well as contact with applicable vessels and reagents. A blank must always be the first sample injected into the system to ensure a clean background signal from the instrument, but it can also be injected after a high concentration standard for the same reason. The resultant signal from the system should only show the signal caused by the injection system and no contamination. For example, the late elution of a component in an IC system in the chromatograph of a blank sample can reveal carryover from the previous injection. Additionally, blanks are used to ensure there is no contamination from the sample preparation method. The results must be fully documented and periodically reviewed to determine if the method is out of control or biased (Currie, 1999; Masson, 2007).

The method performance can be evaluated plotting the above parameters plotted on control charts. Control charts are used to track parameters over time (in both the short term and intermediate term) and identify sources of systematic error and bias (Masson, 2007). Control charts are based on the results of QC standards and allow the operator to quickly evaluate the quality of the data and the performance of the method so that immediate changes may be made to the procedure or results discarded before entering the data stream. Statistical techniques are applied to the results to detect trends and identify their potential source. Basically, control charts are graphical representations of the quality characteristics under investigation (Simonet, 2005). The variable of interest is generally plotted on the y-axis with time or sequential run number on the x-axis. As new control values are generated as part of routine analysis of sample batches, values are added to the control charts for all parameters that characterize the method. Acceptable performance limits can be established for a certain period of time to ensure the method and the results are reliable. Chart lines that correspond to the expected value and the warning limits (generally two standard deviations) and control limits (generally three standard deviations) are typically included on the chart (Masson, 2007).

Over the short term, deviations from the tolerance limits indicate when the method is not meeting the requirements set by the laboratory. The tolerance limits allow the analyst to monitor

the results and either accept the method as in control or conclude that the method is out of control. Several indicators have been proposed to evaluate control samples. When the control result falls within the warning limits, the batch can be classified as in control and the results can be accepted and reported. When the control result falls outside the warning limits, but within the control limit, no action is required provided the next result falls within the warning limits. If the next result does not fall within warning limits, remedial action is required. If the control measurement falls outside the control limits, the batch is considered to be out of control and the analytical results of the batch should be rejected and not reported. It should be noted that statistical control does not imply that the system is performing accurately, only that the method is in control and the system is stable. If the method does not meet the requirements of the analysis or is based on erroneous assumptions, the results will be in error even if there are no statistical variations reported by the control standards. The control standards can only monitor variable factors or random error (Masson, 2007).

Over the intermediate term, the results of control standards may be used to detect changes in performance during routine operations and between various batches of samples. Control charts of data collected over a long period of time may reflect additional variability as a result of homogeneity of samples, precision of the instrument, changing operators, different standards and reagents, and different matrices in different batches. This evaluation of long-term reliability can either establish confidence in the results produced or reveal that the method is not suitable for the analysis and operational conditions need to be modified, a better method introduced, equipment upgraded, or personnel training needed (Masson, 2007).

Internal standards are added to all standards and samples to monitor systematic and/or random error during chemical analyses. Internal standards are comprised of metals that are not expected to be present in the sample and do not interfere with the quantification of the analyte of interest. By monitoring the internal standard signal, drift or other issues such as incomplete ionization of samples can be identified and, in some cases, corrected (Batley, 1999).

2.3.3 Calibration

External calibration is usually done via a calibration curve established by measuring a series of standards of different concentrations that bracket the concentration ranges of the samples (either diluted or undiluted). Typically, a range of standards is produced by serial or individual dilutions of a stock multielement solution. For ICP, standards are acidified with nitric

acid to a pH value generally < 1.5 that ensures the stability of the solutions. For IC standards, no acidification is required. The lowest standard in the series is comprised of the diluting medium only (water) and, for ICP, is acidified. ICP systems exhibit a great linear dynamic range, and the calibration curve should be a straight line. The calibration line of an IC system should also be a straight line, although the concentration range may be much smaller. In cases where the IC calibration line is not straight for a given concentration range, several calibration lines (with a minimum of three calibration points) may be produced and the appropriate line selected for each result. If all points, including the calibration blank, are aligned on this line, then the calibration can be considered potentially viable. For both ICP and IC calibration lines, the curve may only appear to be straight and the errors may seem negligible. In reality, the precise alignment of points, especially at low concentrations, may not be attained and discrepancies can appear. For this reason, CCS should be analyzed to determine the validity of the calibration curve. Most software offers several options to optimize the calibration curve after measurements to ensure good agreement between the 'true' value of a CCS and its measured value (Salomon et al., 2002).

The inadequate choice of calibration procedures can also introduce several errors and uncertainties. This is especially apparent in very sensitive techniques such as ICP-MS that have a large dynamic range. The calibration blank used for repeated calibration curves may strongly influence the results. Small variations in blank values will bring about changes in the slope (b) of the calibration curve, producing greater uncertainty for low concentration analytes (Salomon et al., 2002). A calibration blank (CB) differs from a procedural blank, although both represent all reagents that the samples are in contact with and procedures undertaken. Whereas the procedural blank is used to control for errors and uncertainty, the calibration blank is used during calibration and should be systematically subtracted from sample results (Salomon et al., 2002).

Calibration is often done by linear regression, where a line is fit to a 'best fit', in some defined sense, to a set of calibration data. The independent variable (x) is the known concentration of analytes and the dependent variable (y) is the instrument response. The regression line $y = a + bx$ (where a is the y-intercept and b is the slope of the line) is calculated from the points (x,y) by the method of least squares. This is accomplished by finding the line with the minimum value of the sum of the squared residuals. The regression coefficients are given by:

$$b = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sum(x_i - x_{sum})^2} \quad (1)$$

and

$$a = \bar{y} - b\bar{x} \, . \quad (2)$$

The regression line is defined by finding the values of *a* and *b* that provide the smallest possible value of the sum of the squared residuals:

$$Q = \sum r_i^2 = \sum(y_i - \hat{y}_i)^2 = \sum(y_i - a - bx_i)^2. \quad (3)$$

Two types of suspect data can adversely affect the definition of a regression line: outliers and leverage points. Outliers are anomalies in the dependent variable (instrument response or y) and have the effect of pulling the fitted line towards that outlying value, thus causing the regression line to misrepresent the other (valid) points. Therefore, a visual appraisal of the data should be undertaken to identify these outliers before regression is calculated. Extreme outliers should be removed from the data set and the regression line recalculated. Marginal outliers are more difficult to deal with because their identification and impact can be problematic to determine. Typically, it is advisable to repeat the whole calibration if anomalous data points are encountered.

Leverage points are anomalies in the independent variable (concentration or x). Their distance from other points can draw the fitting line towards them. Even if they are close to the same trend, they can influence the rest of the points and have an undue effect on the regression line. These points should be treated with caution, although they can usually be avoided in calibration.

Correlation, r, is the measure of the strength of the relationship between two variables. A perfect linear relationship between two variables will result in an r value of exactly 1 or -1. The value of r will fall between -1 and 1, regardless of the actual x and y values, and can be calculated using:

$$r = \sum \frac{(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}} \, . \quad (4)$$

Caution should be taken when interpreting the value of r for a set of data because outliers have a strong effect on the calculated value. Also, data sets with an exact functional relationship that is not linear will not necessarily result in values of r that are above zero (Thompson, 1992).

2.4 Data Management

Data management protocols can reduce errors that can be introduced during data processing. The data management protocols ensure appropriate precision, preliminary screening for outliers, and checking of samples that have been flagged. A major source of error involves the recording of signal responses that relate to concentration. During IC analysis, peak heights or areas and the associated baseline and peak resolution can be major sources of error. Most instrument software will draw the baseline on signal peaks, although it is worth checking that this has been done correctly. The maintenance of laboratory records is another important part of data management. Records should enable the traceability of results from the final report back through the method to the original samples or sampling records. This allows the analyst to check for errors in calculation or data transcription that may occur (Batley, 1999).

2.4.1 Uncertainty and Error

A statement of MU must be reported with any results that need to be comparable. This means that results must be traceable to a common primary reference. After methods are validated to show that they are actually measuring what is intended, the quality and reliability of analytical data rests on the comparability of the results for their specific purpose. With the wide variety of types of analytical methods, a key aspect of reliability and validity of results is that they are comparable no matter what their origin. Comparison between different results must include consideration of both concentrations as well as MU. Uncertainty of the results arises from the combination of all uncertainties in the procedure (Taverniers et al., 2004a).

The MU is defined as a parameter associated with the result of the measurement that characterizes the dispersion of values that can be attributed to the measurand. This parameter is generally one SD or the width of a confidence interval. This range or interval represents the range in which the true value lies with a specific probability, after all sources of error have been taken into account. Within this range, the result is considered to be accurate (Taverniers et al., 2004a). The traditional approach to estimating MU is to identify, quantify, and combine all individual sources of uncertainty. This approach of combining all individual uncertainties is

known as the ‘bottom-up’ approach. A more simplified approach is to assess the MU by evaluating individual method-performance characteristic (mainly repeatability and reproducibility), although not all sources of uncertainty (e.g., sample collection, sample preparation, method bias, matrix effects) may be covered by this calculation (Taverniers et al., 2004a).

There are several methods for determining MU but only two will be discussed in this section; bottom-up and top-down. Before calculating MU using either method, all contributions to MU must be identified. This is often accomplished through the use of a flow chart based on the information presented in detail in a SOP. In the case of the bottom-up approach, the standard uncertainties, or standard deviations, of all individual sources of uncertainty are quantified and combined. This method is highly complex because it is difficult to guarantee all sources of uncertainty have been accounted for. The top-down approach is based on data from precision studies, with MU calculated according to:

$$MU = k\frac{SD}{\sqrt{n}}, \tag{5}$$

where k is the coverage factor and has a value of 2 for a level of significance of α = 0.00=5 (at the 95% confidence level) (Konieczka & Namieśnik, 2009).

There is a distinct difference between MU and error. The error of an individual result is the difference between the result and the true value. The value of a known or systematic error can be corrected to a result, meaning that, after correction, the result of an analysis may be very close to the true value. The MU may still be very large as a result of the doubt or limited knowledge about how close the result is to the true value. MU is expressed as a range but is different for different determinations and measurement results, and therefore the value of the uncertainty cannot be used to correct a result. The MU is derived from different error components that are known as ‘sources of uncertainty’ (Taverniers et al., 2004a).

Errors are classically categorized as random or systematic. Random errors generally refer to precision (repeatability, intermediate precision, and reproducibility). Systematic errors are generally attributed to the uncertainty associated with the bias estimate and the calibration. Other contributions to uncertainty include sampling effects, matrix effects, and other assumptions that relate to the measurement method and/or calculations. The errors associated with an analytical method include (Taverniers et al., 2004a):

1) The systematic error associated with the method (method bias).
2) The systematic or random error associated with the laboratory.
3) The systematic error associated with a single run or the random error associated with the variation over several runs.
4) The random error from replicate measurements (repeatability error).

CHAPTER 3
METHODOLOGY

3.1 Principles of the Quality Control Program

All work performed by the U of S Aqueous and Environmental Geochemical Laboratory staff is based on foundational principles that guide practices and procedures. It is through consideration of these principles and adherence to the procedures based upon them that the laboratory produces data of a requisite quality as well as collects and reports these data in a responsible manner.

Laboratory procedures and business practices performed by staff are to conform to ethical standards set out by the University of Saskatchewan (U of S) *Responsible Conduct of Research Policy* (2013). Thereby, the research and scholarly work of members of the U of S is held to the highest standard, is ethically sound, and is conducted in an exemplary fashion. The stewardship of resources is transparent and complies with all U of S and funding agency policies and regulatory requirements. The staff have reviewed this policy and understand the consequences of unethical behavior and actions.

The analytical laboratory seeks to provide the most consistent and cost-effective data of a known quality to provide scientists, planners, policy-makers, and decision-makers with sound, impartial information (Maloney et al., 2005). This is achieved and demonstrated through the development of and adherence to a QCP.

The safety and health of all persons related to the laboratory, including staff participating in field work and sample collection, is protected through engineering controls, standard operating procedures (SOPs), training, and the continued review and revision of the safety program. These actions aim to promote safe practices and habits at all times within the work environment (Maloney et al., 2005). Safety hazards in the laboratory and in the field are managed by understanding the risks and being prepared for them. The safety precautions outlined below, as well as those noted in site-specific training, can help protect the individual, other staff, and laboratory facilities. The following is a list of some of these precautions:

1) All staff must comply with federal, provincial, and local safety regulations as well as adhere to U of S *Safety Codes of Practice* (2012–2013).

2) Material Safety Data Sheets (MSDSs) must be referenced to identify hazards, ensure proper use of personal protective equipment (PPE), and understand the emergency protocols associated with any chemical before beginning work with those chemicals.
3) Staff must utilize appropriate engineered controls such as a fume hood for procedures producing noxious fumes.
4) Staff must identify the locations of safety equipment, including emergency shower and eyewash station, fire extinguisher, spill kit, and emergency exits, before beginning work in a new location.
5) Spills must be cleaned up immediately using the appropriate decontamination procedure.
6) All waste must be disposed of in the appropriate waste streams (i.e., dry hazardous waste boxes and aqueous hazardous waste jugs) in accordance with the U of S *Hazardous Waste Disposal Standard* (2012).
7) Staff must place workplace labels must on all vessels (i.e., bottles, beakers) that contain a solution/solid for more than 1 hour. A workplace label must include the compound(s), the associated hazard(s), name of the generator, date, and a reference to an MSDS.
8) Staff must be aware of the safety concerns regarding sampling that may include steep and unstable ground conditions and remote locations. Plans for sampling and sample preparation should include proper equipment and training of personnel to address potential hazards. Further information is found in the U of S *Fieldwork and Associated Travel Safety Guidelines* (2007).

Environmental compliance of the analytical laboratory is twofold. First, the laboratory participates in and contributes to investigations concerning the natural environment, its resources, and the impact of human activities. Second, the laboratory aims to improve its environmental stewardship by preventing the accidental release of hazardous materials to the environment as outlined in the U of S *Hazardous Waste Disposal Standard* (2012). All laboratory staff are responsible and accountable for complying with the rules and regulations set out by U of S environmental policies and goals and are to apply environmentally safe practices and pollution prevention to all laboratory activities (Maloney et al., 2005).

The analytical laboratory endeavors to be at the forefront of techniques and operations as evidenced by publications, quality of analytical data, and the overall mission to support

investigations undertaken by the federal and provincial governments, the academic community, and industrial sectors (Maloney et al., 2005).

3.2 Quality Control Program and Quality Control Manual

The principal function of a geochemical analytical laboratory is to produce high quality data that are accurate, reliable, and adequate for the intended purpose. The QCP provides the foundational guidelines for data generation. The QCM is one part of an overall QCP, documenting all procedures that may have bearing on the quality of data so that those procedures may be monitored to ensure the specified quality is maintained (Ibe & Kullenberg, 1995; Ministry of Water Land and Air Protection, 2003; Olivares & Lopes, 2012; Sims & Wolf., 1995; Taverniers et al., 2004a)**.** A unique QCM was drafted to document all resources, policies, and procedures that make up the QCP for the U of S Aqueous and Environmental Geochemistry Laboratory. Due to the unique nature of the projects supported by the laboratory, a unique QCM was required.

3.2.1 Organization

The Aqueous and Environmental Geochemistry Laboratory houses several pieces of analytical equipment that are the responsibility of individual operators, as shown in Figure 1.

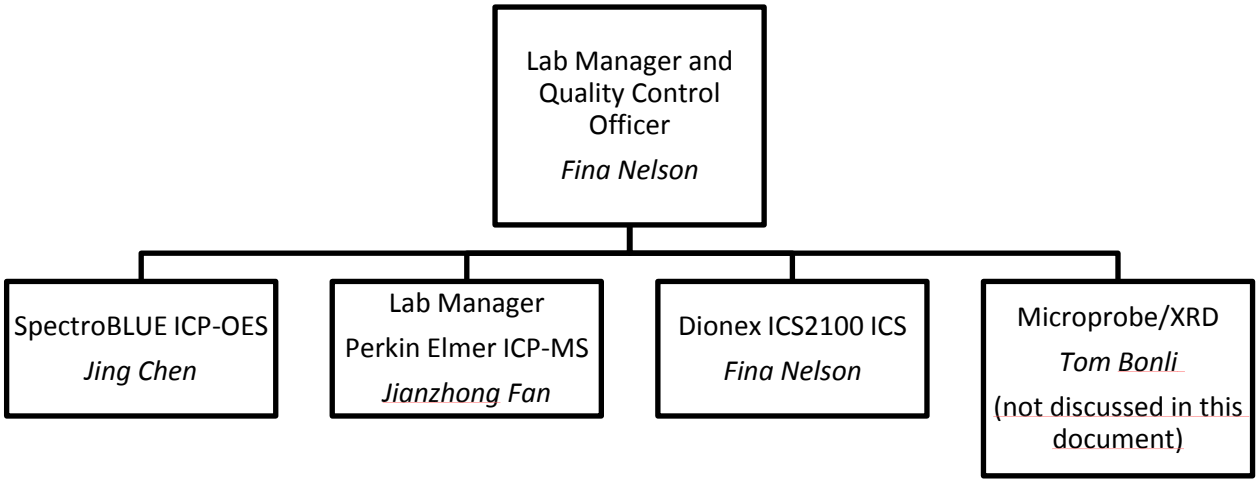


Figure 1. Organizational chart of the Aqueous and Environmental Geochemistry Laboratory.

The QC procedures are conducted by the operators and overseen by the Quality Assurance Officer (QAO) to maintain and improve accuracy, precision, and reliability of data

produced in any laboratory analysis. Operators are responsible for the quality control protocols and criteria for all aspects of laboratory work applicable to that analysis. Methods must first be confirmed using an initial demonstration of laboratory performance approach (see section on SOPs). Each batch of samples reported must be accompanied by the results, including the associated error of the following QC protocols to assess laboratory and instrument performance (see section on SOPs for further explanation and acceptable limits):

- Date of analysis
- Blanks
- Calibration Standards
- CCS
- LFM
- Internal Standards (where applicable)

Reports must also include reference to any problems encountered (e.g., rejected analytical batches, loss of sample). Control charts are generated by the QAO to monitor the performance of an analytical method, reagent and standard quality, analyst technique, and the status of any in-house references being used. If reported values do not meet QC requirements, SOPs are reviewed and any necessary modifications made.

The QAO compares results from different methods (ICS, ICP-OES, and ICP-MS) within the laboratory as well as submitting samples to external laboratories (Saskatchewan Research Council Analytical Laboratory in Saskatoon (SRC) and ALS Environmental Laboratory in Edmonton (ALS)) to compare with results generated in the laboratory. These results are compared to evaluate the quality of the data produced by the Aqueous and Environmental Geochemistry Laboratory and either ensure agreement between methods or determine which method is more appropriate for each application.

3.2.2 Managing Records

Log books are maintained for each instrument and analytical system and are the property of the laboratory. A log book should include, but is not limited to, the following information: instrument identification, serial number, date of calibration or installation, any modifications made to the system, operator, calibration conditions, analytical file information, sample

identifiers, dilutions (when applicable), and dates of analysis. The log books are kept with the instrument for a period of no less than 5 years (Maloney et al., 2005).

Records of calibration are kept for each analysis batch and reported with the data to the QAO. These records must also include any references to abnormalities or modifications to the procedures outlined in the SOPs (e.g., exclusion of outliers).

Internal chain of custody (COC) forms are generated by the QAO when samples are received by the laboratory and transferred to the operator. The operator is responsible for updating the COC form when samples are analyzed and when they are transferred back to the QAO. This form will track the sample during analytical testing. Any deviations should be recorded. An example of an internal COC is below in Fig. 2.

Chain of Custody Form – **Aqueous and Environmental Geochemistry Laboratory: ICP-MS**						
Sample ID	Received by FN	Received by JF	Analysis Date	Location Initial	Location Intermediate	Location Final
10471	09-Jun-13	10-Jun-13	12-Jun-13	Fridge A	Geol 211	Cooler
10472	09-Jun-13	10-Jun-13	12-Jun-13	Fridge A	Geol 211	Cooler

Figure 2. Example of an internal COC form.

3.2.3 Standard Operating Procedures

SOPs are an integral part of the QCP and include four basic sections (Winter et al., 1993):

- Section 1. Sample Handling: The SOP must contain specific instructions for the selection of sample containers as well as procedures for collection, preservation, transportation, and storage of samples.
- Section 2. Equipment Requirements: The SOP must contain detailed instructions on glassware cleaning, purity requirements for reagents, equipment and apparatus performance specifications, and equipment performance verification and documentation.
- Section 3. Sample Analysis: The SOP must detail all calibration and QC requirements of the analytical procedure, including an initial demonstration of

laboratory performance, protocols for contamination control, calibration order (e.g., linear), calibration concentration/signal range, method precision, method bias, and other performance criteria.

- Section 4. Data Review and Statistics: The SOP must contain instructions on evaluation of control standards and sample results and statistical methods.

Each of these four sections are described in detail below.

Section 1 of the SOP is comprised of sample handling protocols, which are designed to minimize the alteration of analytes of interest in both the field and the laboratory. These strict precautions protect sample (analyte) integrity. Inadvertent addition or loss of analytes can occur during sample collection and transportation. Several considerations prior to sample collection can mitigate these effects:

1) Methods blanks (MB) should be included in the sampling scheme. MB are samples of deionized (DI) water that are processed in the same manner as other samples. Three percent of the sample bottles are filled with DI water and processed identically to the samples and then analyzed to determine contamination caused by the method or sample bottles.
2) Milli-Q (18 Ω, Millipore, USA) DI water should be used for all dilutions and solution preparations.
3) All labware must be thoroughly cleaned and rinsed. Labware should be washed in tap water, rinsed three times in DI water, soaked for 4 hours in 10% nitric acid, rinsed three times in DI water, soaked for 4 hours in DI water, and air dried. Labels are to be removed prior to acid bath. DI water is to be used for final rinses of labware and sample collection and filtration equipment.
4) Trace grade chemicals must be used for ICP-MS and ICP-OES analyses.
5) All samples should be collected using bottle and preservation techniques outlined in to Table 1 and transported and stored under cool and dark conditions.

Table 1: Sample handling details.

Sample	Bottle Type	Preservation	Minimum Volume
ICS	20 mL LDPE scintillation vials with polyethylene cone liner urea cap	Filtered	1 mL
ICP-OES	30 mL LDPE	Filtered, 2% v/v HNO_3	8 mL
ICP-MS	30 mL LDPE	Filtered, 2% v/v HNO_3	1 mL
Alkalinity	60 mL HDPE	None	20 mL
Se Speciation	20 mL Brown PP	Filtered, Frozen	1 mL
Water Isotopes	20 mL LDPE scintillation vials with polyethylene cone liner urea cap transferred into 1.5 mL glass vials	Filtered	1 mL

Samples should be filtered as soon as possible after sample collection. Filtering removes particulates that are in suspension but not part of the aqueous phase. An exception is the measurement of alkalinity, which should be done on unfiltered samples because suspended constituents contribute to the acid neutralization potential of the sample. Filtration of water samples is performed either using a Millipore® 142 mm Hazardous Waste Pressure Filter System and Millipore® Durapore® PVDF 0.45 µm hydrophilic membrane filters for larger sample volumes (> 500 mL) or a polypropylene syringe and Acrodisc® PES 25 mm 0.45 µm syringe filters for smaller sample volumes (< 500 mL). Depending on the goals of the project, a filter pore size smaller than 0.45 µm may be required because colloids may still pass through the filter and carry sorbed species with them and therefore not be truly "dissolved" species only (Hassellov & von der Kammer, 2008). Filter apparatuses should be washed, rinsed with DI water three times, and dried before use. Filter tubing and funnels should be made of surgical silicone, Tygon, or other inert material and cleaned thoroughly prior to use. Care should be taken that water samples to be analyzed for trace metals do not come into contact with stainless steel. Also, for safe operation of a pressure filter, the pressure should be kept as low as possible and not

exceed 30 psi (Pickering, R. J. (Quality of Water Branch, USGS)). Samples are diluted with Milli-Q (18 Ω, Millipore, USA) DI water and ICP-MS grade reagents are used for all ICP-MS and ICP-OES sample preparation.

Section 2 is comprised of all equipment used during analysis and the records associated with that equipment. An instrument log that records all problems, repairs, and maintenance actions for all major equipment is kept by the operator. Operators are also required to keep calibration logs for support equipment (Fig. 3).

Type of Equipment	Maximum Period between Successive Calibrations	Procedures
Automatic burettes, dispensers, and pipettes	Initial and three months	Accuracy and repeatability of volumes in use
Balances	Initial calibration and three yearly calibrations	Calibration using certified masses
Conductivity and pH meter	Each use	Check using appropriate standards in each of the scale ranges of the meter in use

Instrument Calibration Record

Instrument No.: Instrument Model:

Location: Serial Number:

Date	Standard used for calibration	Measured value(s)	Pass/Fail	Recalibrated instrument (Y/N)	Analyst

Note: Instrument should be recalibrated if measured value for a particular standard deviates from the standard check acceptable value.

Figure 3. Examples of support equipment and calibration records.

Section 3 is comprised of the actual analytical procedures used in routine analysis. Before routine analysis is conducted, an initial demonstration of laboratory performance must be conducted. The initial demonstration of performance is used to characterize the instrument performance (determination of linear calibration ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) (Hautman, 1997; Martin, T.D., Brockhoff, C.A., Creed, 1994). An initial demonstration of laboratory performance includes the following aspects:

1) Linear Dynamic Range (LDR) – To determine the LDR, successively higher standard concentrations of the analyte are analyzed until the observed analyte concentration is no more than 10% below the stated concentration of the standard.
2) Method Detection Limit (MDL) – An MDL should be established for all analytes, using reagent (blank) water fortified at a concentration three to five times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over at least three separate days. The MDL = t × SD, where t = Student's t for 99% confidence. MDLs should be determined every six months or when any major changes in background, instrument response, or personnel occur.
3) Quality Control Sample (QCS) – When beginning a method and on a quarterly basis, verify the calibration standards and acceptable instrument performance with the preparation and analysis of a QCS. The QCS should be prepared from a separate source than the calibration standards and can be used regularly as a CCS.

Total Elemental Analysis by ICP-MS

Total elemental analysis is performed using a Perkin Elmer NexION300D ICP-MS coupled to a Perkin Elmer S10 Autosampler. The system is optimized for maximum sensitivity and minimum oxide and doubly-charged ion formation. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. This correction is achieved by the use of an IS and Perkin Elmer software. Standard addition and external standardization is used for calibration and quantification. Calculation is completed either online using NexIon software or offline using an Excel spreadsheet. The precision of this method is 5 to 10% depending on elements and concentration. The analysis is performed similar to (Longerich, Jenner, Fryer, & Jackson, 1990; Stefanova, Kmetov, & Canals, 2003; Test Methods for Evaluating Solid Waste, 2007), as follows:

1) Individual stock solutions (1000 mg/L) are purchased from SCP Science (Baie-d'Urfé, QC).
2) All samples and standards are brought to room temperature before conducting sample analysis. An aliquot of well mixed, homogenous aqueous is accurately weighed or measured for sample processing. All samples are made ready for analysis by the

appropriate addition of nitric acid (2% v/v) and known amounts of IS (selected from 50 ppb Be and 10 ppb Ge, Rh, In, Tb, and Bi; SCP Science; Baie-d'Urfé, QC).

3) Samples are diluted gravimetrically to within the established linear dynamic range.
4) A mass calibration check is performed using a tuning solution and adjusted if change is > 0.1 atomic mass units (amu). A resolution check is performed and adjusted if > 0.75 amu at 5%. Instrument stability must be demonstrated by running the tuning solution a minimum of five times with a resulting percent difference (%D) < 5%.
5) The instrument operating conditions (Table 2) are optimized.
6) For every batch, six calibration solutions (CALs) are analyzed every eight samples. Concentrations of CALs vary from 1 to 15000 ppb. A CB is also analyzed. CAL solutions are prepared fresh from stock solutions every two weeks.
7) A minimum of three replicate integrations is required for all data acquisition. The average of the integrations is used for instrument calibration and data reporting. Solutions are aspirated for 30 s prior to the acquisition of data to allow equilibrium to be established.
8) Four CCS solutions are analyzed to verify the instrument is reporting within 5–10 %D of calibration.
9) To provide confidence in data, it is suggested that all actual samples should be randomized to spread out any temporal systematic biases such as instrument drift (Birke et al., 2010).
10) Samples are analyzed with 10% of samples being Dup and an LRB in each batch. The flush between samples is 150 s.
11) All masses that might affect data quality are monitored during the analytical run. Interference corrections are made by Perkin Elmer default NexIon software and EPA Method 6020A (Test Methods for Evaluating Solid Waste, 2007).
12) Field reagent blank (FRB) solutions and LRB solutions are carried through the procedure in the same fashion as samples.
13) For the analysis of barium (Ba) in samples having varying and unknown $SO4^{2-}$ concentrations, analysis should be completed as soon as possible after sample preparation.

Table 2: ICP-MS instrumental operating conditions.

Nebulizer:	Meinhard glass microconcentric
Spray Chamber:	Glass cyclonic
Triple Cone Interface Material:	Nickel/Aluminum
Plasma Gas Flow:	16.0 L/min
Auxiliary Gas Flow:	1.2 L/min
Nebulizer Gas Flow:	0.93 L/min
Sample Uptake Rate:	0.5 mL/min
RF Power:	1350 W
Integration Time:	600 – 1500 ms
Replicates per Sample:	3
Mode of Operation:	Standard, Collision (He), Reaction (NH_3)

Cleaning Procedure for ICP-MS Support Equipment

1) Teflon vials and caps are immersed in clean tap water immediately after sample transfer. Teflon containers are hand washed for obvious dirt.
2) Two acid baths consisting of 4 L glass beakers with a glass cover lens are generated. The acids consist of 6M HCl (Acid Bath #1) and 8M HNO_3 (Acid Bath #2) and are generated from reagent grade acids and placed on hot plates set at 50–80 °C.
3) Labware is rinsed with Milli-Q water and soaked in Acid Bath #1 for 3 days. Labware is removed from Acid Bath #1 with Teflon coated tongs, rinsed with Milli-Q water, and soaked in Acid Bath #2 for 3 days. Labware is removed from Acid Bath #2 with Teflon coated tongs, rinsed with Milli-Q water, dried, and stored in clean plastic containers.

Analysis of Major Cations and Select Trace Metals by ICP-OES

The analysis of aqueous sample for the quantification of major cations including sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), P, and sulfur (S) and select trace metal including Se, As, and cadmium (Cd) is performed using a radial view SpectroBLUE ICP-OES coupled to a CETAC ASX-520 Autosampler. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. This correction is achieved by the use of an IS and Spectro software. Various interferences must be

also considered and addressed using a spectral interference check (SIC) solution. External calibration is used for the determination of concentrations. The equipment is controlled and conductivity recorded using Spectro Smart Studio software. Precision of this method is 5–10% depending on elements and concentration. The analysis is performed similar to methods described in EPA Method 200.7 and 300.1 (Hautman, 1997; Martin, T.D., Brockhoff, C.A., Creed, 1994):

1) Individual cation stock solutions of 10,000 or 1000 mg/L are purchased from SCP Science (Baie-d'Urfé, QC).
2) All samples and standards are brought to room temperature before conducting sample analysis. An aliquot of well mixed, homogenous aqueous sample is accurately measured for sample processing. All samples are made ready for analysis by the appropriate addition of nitric acid (2% v/v) and IS containing 2 ppm Sc.
3) Samples are diluted gravimetrically to within the established linear dynamic range.
4) The instrument operating conditions (Table 3) are optimized.
5) For every batch, five CAL solutions prepared from stock solutions are analyzed. A CB is also analyzed.
6) A minimum of three replicate integrations are required for all data acquisition. The average of the integrations is used for instrument calibration and data reporting. Solutions are aspirated for 45 s prior to the acquisition of data to allow equilibrium to be established.
7) Four CCS solutions are analyzed to verify the instrument is reporting within 5–10 %D of calibration.
8) FRB and LRB solutions are carried through the entire process. LRBs are analyzed every 20 samples.
9) Samples are analyzed, with 10% of samples being Dup and LRB. The flush between samples is 45 s.
10) To provide confidence in data, all actual samples should be randomized to spread out any temporal systematic biases such as instrument drift.
11) All elements that might affect data quality are monitored during the analytical run. Interelement spectral interference correction is verified using SIC solutions.

Table 3: ICP-OES instrumental operating conditions.

Flow Rate:	2 mL/min
RF Power:	1400 W
Nebulizer	Glass Cross-flow
Spray Chamber:	Glass Scott
Auxiliary Gas:	0.85 L/min

Analysis of Major Anions by IC

The analysis of aqueous samples for the quantification of major anion (F, Cl, NO_2, Br, NO_3, PO_4, SO_4) concentrations is performed using a Dionex ICS2100 coupled to a Dionex AS-AP Autosampler. A Dionex IonPac AS9-HC 2×2 mm exchange column is used with a 9.00 mM K_2CO_3 eluent for the separation of common anions. A conductivity detector is used after suppression (Thermo Scientific ASRS 300 2 mm regenerating suppressor). The equipment is controlled and conductivity recorded using Chromeleon 7.2 software. The analysis is performed similar to methods described in EPA Method 300.1 (Hautman, 1997):

1) Mixed anion standard stock solutions (100 ppm F, 2000 ppm Cl, 100 ppm NO_2, 250 ppm Br, 500 ppm NO_3, 100 ppm PO_4, 2000 ppm SO_4) are purchased as certified solutions (Ricca Chemical Company; Arlington, Texas).
2) Eluent is prepared automatically from a certified K_2CO_3 cartridge (Thermo Fisher Scientific; Sunnyvale, California).
3) All samples and standards are brought to room temperature before conducting sample analyses.
4) Seven CAL solutions, two CCSs, one LRB, and any required quality control samples are prepared gravimetrically once a week.
5) ICS operating conditions (Table 4) are optimized during method development and validation and not adjusted with each batch.
6) Eluent is pumped through the system until a stable baseline is achieved (approximately 45 min).
7) One LRB is analyzed at the beginning and end of each queue to verify the procedure is free of contamination. LRB and FRB solutions are carried through the procedure in the

same fashion as samples. Additional LRB solutions are included mid-batch if samples with relatively high concentration (>400 mg/L) are being analyzed.

8) Seven CALs at the beginning of the week and two CCSs at the beginning and end of each batch are analyzed to verify the instrument is reporting within 5–10 %D of calibration.
9) Two calibration lines are generated (one for high concentration and one for low concentration) by plotting the peak area response for standards against concentration.
10) Samples are diluted gravimetrically to within the calibration range.
11) Samples are analyzed, with 10% being Dup and LRBs.
12) Using the area of each peak, the concentration of the samples is calculated using the appropriate calibration line. Peak areas must be within the calibration range. If peak areas are too high, the analysis is repeated with a higher dilution factor.
13) After each batch of samples, the pump is rinsed with DI water to prevent crystallization of eluent in the pump.

Table 4: Anion ICS operating conditions.

IC model:	Dionex ICS-2100
Autosampler model:	Dionex AS-AP
Software:	Chromeleon 7.2
Exchange column model:	AS9-HC 2×2 mm exchange column
Suppressor model:	ASRS 300 2 mm regenerating suppressor
Flow Rate:	0.25 mL/min
Internal Pressure:	~2000 psi
Column Temp:	30 °C
Cell Heater Temp:	35 °C
Injection Volume:	0.25 mL
Suppressor:	12 mA
Detection:	Suppressed conductivity
Eluent Generating Cartridge Strength:	9 mM
Background:	0 uS (autozero from ~30 uS)
Run Time:	26 min

Section 4 of an SOP consists of data review and statistical analysis of QC solutions during data processing to determine method and instrument performance. QC solution results are verified to be within acceptable limits before the results of unknown samples are evaluated. Necessary statistical equations are presented in Section 3.3. The following are descriptions and acceptable limits of QC standards used:

1) A CB consisting of a volume of LRB is acidified with the same acid matrix as the calibration standards and is used as a zero standard when calibrating the ICP-MS and ICP-OES instruments.
2) For every batch of` ICP-MS, ICP-OES, and ICS analysis, CCS solutions are analyzed to verify the calibration line and instrument performance. Results must be within 5–10 %D of the reported values of the analytes. For the concentration range between the MDL and 10×MDL, the %D may be higher. CCS solutions are made from RM or CRM solutions from a separate source material than the CAL standards.
3) The CAL solutions are prepared by the dilution of stock standard solutions and serial dilutions. The CAL solutions are used to calibrate the instrument response with respect to an analyte concentration. A calibration line for ICP-MS, ICP-OES, and ICS analyses must be based on at least three CAL solutions.
4) A minimum of 10% of samples are Dup and a relative percent difference (RPD) is calculated. Reported RPD should be no more than 5–10% for ICP-MS, ICP-OES, and ICS analyses.
5) For every new batch of bottles or vessels, reagent water is placed in a sample bottle and treated as a sample in all respects, including shipment, exposure to field conditions, storage, preservation, and all analytical procedures. Results must be below the MDL for ICP-MS, ICP-OES, and ICS analyses.
6) For ICP-OES and ICS analyses, an LFM solution is generated by the addition of a known amount of analyte (3–5×expected concentration) to 10% of field samples within an analysis batch. It is recommended that stock solutions for calibration standards be used for preparation of the LFM. %Recovery should be 75–125%.
7) An LRB consists of DI water and must be analyzed at least once per batch. Values must not exceed MDL concentrations.

8) For ICP-MS and ICP-OES analysis, an IS solution is used to monitor changes in signal response from the instrument with time. An IS solution is generated by the addition of pure analyte(s) of a known amount(s) to all standards and samples. The IS must be an analyte that is not a sample component. For a full range ICP-MS scan, a minimum of three internal standards must be used. The absolute response of any one IS must not deviate more than 60–125% of the original response in the calibration blank.
9) A tuning solution is used for ICP-MS instrument tuning and mass calibration prior to analysis. The solution contains 1 µg/L of Ba, Be, Ce, Co, Fe, In, Mg, Pb, and U.

3.3 Statistical Methods

Mathematical statistics is a very useful tool for analysts because it reveals characteristics of a population, such as the exactness of a given result and whether it meets DQOs. These characteristics are presented as numbers that can easily be compared. The two main measures used to characterize the results in this thesis are the measure of location and the measure of dispersion (Konieczka & Namieśnik, 2009).

The measure of location involves the use of one value to characterize the general level of the population. One of the most useful measures of location is the arithmetic mean:

$$x_m = \frac{\sum x_i}{n}, \tag{6}$$

where x_m is the arithmetic mean, x_i is a single value in the population, and n is the number of values in the population (Konieczka & Namieśnik, 2009).

Two of the most useful measurements of dispersion, or variability, are %D and RPD. The %D is the difference between the measured or found value ($x_{f)}$ and the true value (x_t):

$$\%D = \frac{x_t - x_f}{x_t} \times 100\%. \tag{7}$$

The RPD is the difference between two values, x_1 and x_2, in which one number is no truer than the other and therefore is expressed in absolute terms:

$$RPD = \left|\frac{x_1 - x_2}{x_m}\right| \times 100\%. \tag{8}$$

The %Recovery is calculated for LFM samples and is calculated from the concentration measured in the LFM (C_{LFM}), concentration measure in the unfortified sample (C_s) and the known amount added to the LFM (C_A) using:

$$\%Recovery = \left|\frac{C_{LFM}-C_S}{C_A}\right| \times 100\%. \quad (9)$$

(American Public Health Association, American Water Works Association, & Water Environment Federation, 1999).

To reduce the influence of outlying results and provide statistics that describe the distribution of the central part of the data, outliers should be rejected from the population (Thompson, 1992). The Hemple test, sometimes also called Huber's test, can be used to detect outliers. Its aim is to detect outliers in a given set by setting a limit to which values can be compared. If a result lies outside of the limit, it is considered an outlier. This test can be applied to a population of CCS values with respect to the known or "true" value of a population of %D values, or to a population of replicates with respect to RPD (Konieczka & Namieśnik, 2009). The following steps are used to determine the outlier limit:

1) Calculate the median of the values.
2) Calculate the absolute deviation, r_i, from the median for each result; $r_i = (x_i - \text{median})$.
3) Calculate the median of the r_i.
4) Calculate the outlier limit as 4.5× the median of the absolute deviations.

Another useful tool to evaluate water data quality is ion balance. Surface and ground waters are electrically neutral, and therefore the anion and cation sums, when expressed as milliequivalents per liter (meq/L), should be equal. This relationship is a means for evaluating analytical techniques and an indication of the accuracy of water analysis data. The relationship can be obtained using the charge-balance equation and deviations from equality expressed as:

$$CBE = \frac{\sum zm_c - \sum zm_a}{\sum zm_c + \sum zm_a} \times 100\% \quad (10)$$

where CBE is the charge balance error expressed in equivalents per million, z is the ionic valence, m_c is the molality of cation species, and m_a the molality of anion species (Freeze and

Cherry, 1979). The CBE for a single chemical analysis is not a reliable gauge of the accuracy of that analysis, but the CBE for a group of analyses becomes more credible (Fritz, 1994).

The direction (positive or negative) of the error is informative is revealing what type of error has occurred. That is, a positive CBE indicates either an over reporting of cations or an under reporting of anions. Positive CBEs are commonly related to alkalinity measurements. If the sample is supersaturated with respect to calcite and/or dolomite, it is likely carbonate minerals will precipitate and collect at the bottom of the bottle. When alkalinity is then measured in the laboratory, alkalinity will be under reported. In the acidified aliquot of the sample analyzed for cations, the carbonate will not precipitate and Ca and Mg concentrations will be accurately reported (Fritz, 1994).

The value of the CBE can be misleading in cases where there are large positive and negative errors. These errors will be averaged to give a near zero when the absolute errors are quite high. Therefore, the CBE should also be treated in terms of the absolute value of the error when calculating the overall error in a population of analyses (Fritz, 1994):

$$|CBE| = \left|\frac{\sum zm_c - \sum zm_a}{\sum zm_c + \sum zm_a}\right| \times 100\%. \quad (11)$$

CHAPTER 4
QUALITY CONTROL RESULTS

4.1 ICP-MS

Analyses were conducted according to the SOP for total elemental analysis by ICP-MS described in Chapter 3. Although a full range of elements were analyzed, only the elements of interest (Ca, Mg, K, Na, P, Ba, Se, As, and Cd) are presented here. All other elemental concentrations were not integral to current projects or did not overlap with analyses from an alternate method. Duplicate samples were collected for 10% of samples when possible (Hautman, 1997). Blind duplicates (BDup) were Dup prepared during aqueous extraction (leaching) of samples and were labeled with only the date of extraction. The operator was unaware of the sample identification number. Acceptable limits for RPD and %D were taken from EPA Method 6020A (Test Methods for Evaluating Solid Waste, 2007) and acceptable limits for outliers from (Konieczka & Namieśnik, 2009). These limits were adapted as DQOs for total elemental analysis by ICP-MS in this laboratory.

The initial demonstration of laboratory performance consisted of determining the linear dynamic range, MDL, and the statistical analysis of QC solutions including CCSs, Dup, and BDup. Statistics including RPD, %D, x_m, SD, MU (based on Dup), and number of outliers are presented for all elements of interest (Table 6). Only select plots are presented for example purposes; all other plots can be found in Appendix A. Although the MDL for a full range of elements was calculated, only results for the elements of interest are presented in Table 5.

With respect to the linear dynamic range, the NexION 300D SimulScan detection system operates from < 0.1 to ~ 10^{10} counts per second (cps). This provides over 10 orders of magnitude of linear dynamic range in a single continuous scan. If the detector is saturated with counts over this amount, the software reports "Saturation" and dilution is required. The concentration associated with the detection of 10^{10} cps varies with element, but is typically in the range of 100 ppm.

Table 5: ICP-MS MDL for elements of interest.

	Ca mg/L	**Mg** mg/L	**Na** mg/L	**K** mg/L	**P** mg/L	**Ba** mg/L	**Se** mg/L	**Cd** mg/L	**As** mg/L
MDL	0.005	0.001	0.0015	0.0015	0.001	0.0001	0.0005	0.00001	0.0001

The calculated MUs for all analytes of interest were < 5.00% at the 95% confidence interval. The results of CCS analyses were within DQOs for %D but high concentration CCS results for Mg (10.0 mg/L) and low concentration results for As (0.005 mg/L) had more outliers than acceptable. The source(s) of the high number of Mg outliers is unclear and matrix interference is likely the source of the As outliers as it is a common challenge for As quantification. The results of Dup analyses by ICP-MS were also within DQO for RPD but Na, K, P, Se, and As had more outliers than acceptable. The source(s) of the high number of Dup Na and K outliers is unclear, although it is suspected that the high number of P, Se, and As outliers were related to MDL, matrix interferences and the low degree of ionization (discussed below). The results of BDup analyses had more mixed results, with Ca, Mg, Na, K, and Se performing within the DQO for RPD but P, Cd, and As above acceptable limits of RPD. Although the concentrations for P BDup were not particularly low (> 10×MDL), there appeared to be a relationship between RPD and concentration (Fig. 4). As concentrations were < 10.0 ppb and both P and As results are likely affected by interference and a lower degree of ionization. There did not appear to be a relationship between RPD and concentration for Cd BDup, but most Cd concentrations were < 10×MDL (Fig. 5). Therefore, the high RPD results are also suspected to be related to the MDL and interference.

Interferences are especially influential at low concentrations because of the increased background noise has a greater effect on accurate signal quantification. The quantification of P is affected by the presence of polyatomic $^{14}N^{16}O^{1}H^{+}$ and $^{15}N^{16}O^{+}$ interferences which overlap with its only isotope (m/z = 31). Common polyatomic interferences affecting As are $^{40}Ar^{35}Cl^{+}$, $^{40}Ca^{35}Cl^{+}$, and less frequently $^{59}Co^{16}O$, Sm^{2+}, and Nd^{2+} (Hill, 2007). The two isotopes of Se which are analyzed (^{78}Se and ^{82}Se) are effected by $^{40}Ar^{38}Ar^{+}$ and $^{38}Ar^{40}Ca^{+}$in the case of ^{78}Se, and $^{40}Ar^{42}Ca^{+}$ and $^{34}S^{16}O_3{}^{+}$ in the case of ^{82}Se (May & Wiedmeyer, 1998). As a result of the interferences with Se, analyses are done in collision mode. The collision cell uses Kinetic Energy Discrimination (KED) to remove many of the simple argon-based polyatomic interferences using the non-reactive gas He (Bosnak, 2007; Vonderheide, Meija, Montes-Bayón, & Caruso, 2003). Collision mode is not used for P or As analyses and instead the instrument software corrects for these interferences using the signal of one of the other interferents isotopes. For example, the signal from $^{37}Cl^{40}Ar^{+}$ is used to correct for interferences from $^{35}Cl^{40}Ar^{+}$ (Hill, 2007).

In addition, the relatively high ionization potential of P, As, and Se also make these elements some of the most challenging elements to analyze in an argon plasma. As a result of these high ionization potentials (10.5, 9.79, and 9.75 eV for P, As, and Se, respectively) the degree of ionization is lower. Under standard operating conditions, approximately 30–80% of P, As, and Se atoms are ionized in the plasma, therefore reducing the analyte signal. This low degree of ionization also effects ICP-OES determinations (Hill, 2007).

Most of the QC results that to do not meet DQOs appeared to have some relationship with concentration, with higher numbers of outliers or high RPD or %D values at lower (< 10×MDL) concentrations, as expected. The results presented in Table 6 indicate that the method and instrument are performing within DQOs, at relatively higher concentrations.

Table 6: Results of QC analyses by ICP-MS and DQOs for elements of interest.

ICP-MS	Ca	Mg	Na	K	DQO
MDL	0.005 mg/L	0.001 mg/L	0.0015 mg/L	0.0015 mg/L	To be determined by laboratory/study
Dup	x_m RPD = 1.31% SD = 1.09% MU = 0.27% n = 66; outliers = 0	x_m RPD = 1.49% SD = 1.25% MU = 0.31% n = 66; outliers = 1	x_m RPD = 2.69% SD = 2.15% MU = 0.53% n = 66; outliers = 7	x_m RPD = 2.37% SD = 1.64% MU = 0.41% n = 65; outliers = 7	RPD < 25% 2 outliers in 20 analyses
BDup	x_m RPD = 10.3% SD = 5.06% n = 27	x_m RPD = 5.94% SD = 4.28% n = 25	x_m RPD = 6.80% SD = 5.58% n = 25	x_m RPD = 11.5% SD = 7.21% n = 24	Same as Dup
High CCS	x_m %D = 3.79% SD = 2.80% n = 58; outliers = 1 Bias: positive	x_m %D = 4.66% SD = 3.12% n = 55; outliers = 7 Bias: positive	x_m %D = 3.85% SD = 2.45% n = 57; outliers = 2 Bias: negative	x_m %D = 4.06% SD = 2.73% n = 54; outliers = 5 Bias: negative	%D < 10% 2 outliers in 20 analyses
Low CCS	x_m %D = 3.83% SD = 3.40% n = 35; outliers = 3 Bias: positive	x_m %D = 5.64% SD = 3.36% n = 51; outliers = 5 Bias: positive	x_m %D = 3.33% SD = 2.67% n = 54; outliers = 2 Bias: negative	x_m %D = 4.17% SD = 2.73% n = 61; outliers = 0 Bias: positive	Same as High CCS

Table 6: (continued).

ICP-MS	P	Ba	Se	Cd	As
MDL	0.001 mg/L	0.0001 mg/L	0.0005 mg/L	0.00001 mg/L	0.0001 mg/L
Dup	x_m RPD = 3.79% SD = 2.50% MU = 0.62% n = 66; outliers = 10	x_m RPD = 0.878% SD = 2.15% MU = 0.53% n = 66; outliers = 0	x_m RPD = 3.54% SD = 3.12% MU = 0.79% n = 62; outliers = 7	x_m RPD = 17.9% SD = 16.8% MU = 4.9% n = 48; outliers = 0	x_m RPD = 14.5% SD = 9.59% MU = 2.4% n = 62; outliers = 7
BDup	x_m RPD = 79.5% SD = 39.4% n = 27	x_m RPD = 8.47% SD = 11.6% n = 27	x_m RPD = 14.1% SD = 10.4% n = 27	x_m RPD = 25.7% SD = 23.7% n = 18	x_m RPD = 31.2% SD = 31.8% n = 27
High CCS	x_m %D = 4.73% SD = 2.57% n = 57; outliers = 1 Bias: negative	x_m %D = 3.57% SD = 2.72% n = 57; outliers = 3 Bias: positive	x_m %D = 3.45% SD = 2.79% n = 6; outliers = 1 Bias: positive	n.a.	n.a.
Low CCS	n.a.	x_m %D = 3.57% SD = 2.72% n = 67; outliers = 4 Bias: positive	x_m %D = 4.46% SD = 3.28% n = 62; outliers = 4 Bias: positive	x_m %D = 7.84% SD = 1.89% n = 23; outliers = 2 Bias: positive	x_m %D |= 6.44% SD = 2.44% n = 23; outliers = 4 Bias: positive

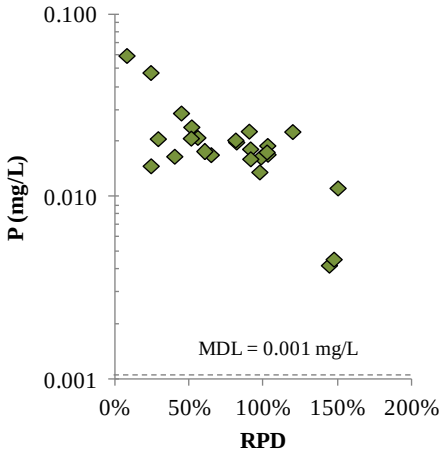


Figure 4. Control chart for selected BDup P analyses by ICP-MS showing a relationship between RPD and concentration.

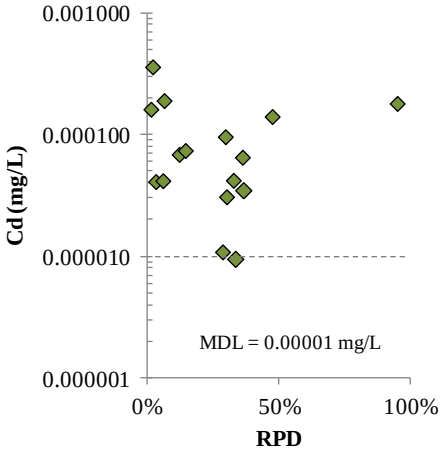


Figure 5. Control chart for selected BDup Cd analyses by ICP-MS showing the 14 of 18 analyses < 10×MDL.

4.2 ICP-OES

Analyses were conducted according to the SOP for analysis of common inorganic cations (Ca, Mg, K, Na, and P) and select trace metals (Se, As, and Cd) by ICP-OES as described in Chapter 3. Although As was analyzed, results are not presented because sample concentrations were below the MDL. Acceptable limits for RPD were taken from EPA Method 200.7 (Martin, T.D., Brockhoff, C.A., Creed, 1994) and acceptable limits for outliers from (Konieczka &

Namieśnik, 2009). Limits for Dup RPD were not specified by EPA Method 200.7; therefore, the limit for CCS %D was used. These limits were adapted as DQOs for total elemental analysis by ICP-OES in this laboratory.

The initial demonstration of laboratory performance was the same for ICP-OES as for ICP-MS, with the exception of LFM analyses conducted by ICP-OES. Statistics including RPD, %D, x_m, SD, MU (based on Dup), %Recovery, and number of outliers are presented for all elements of interest (Table 8). As with ICP-MS results, only select plots are presented for example purposes and all other plots can be found in Appendix A. The LDR and MDL for all analytes measured by ICP-OES were determined and are presented in Table 7.

Table 7: ICP-OES LDR and MDL for elements of interest.

	Ca mg/L	**Mg** mg/L	**Na** mg/L	**K** mg/L	**P** mg/L	**S** mg/L	**Se** mg/L	**Cd** mg/L	**As** mg/L
MDL	0.019	0.004	0.003	0.0009	0.004	0.018	0.004	0.0003	0.004
LDR	MDL–500	MDL–500	MDL–50	MDL–50	MDL–10	MDL–2000	MDL–1	MDL–1	MDL–1

The MUs of the analytes of interest were all < 6.83% at the 95% confidence interval. The results of CCS analyses by ICP-OES were within DQOs for %D and all analytes had acceptable numbers of outliers. The results of Dup analyses were also within DQO for RPD. Dup results for Ca, Mg, Na, K, and S had an acceptable number of outliers and Dup results for Cd had too small of a population to determine statistical outliers. Dup results for P and Se had more outliers than acceptable most of which were < 10×MDL; these are likely related to analyte MDLs and the low degree of ionization. The BDup results for Ca, Mg, Na, K, S, and Se were within DQOs for RPD; the single result available for Cd was within the DQO for RPD. The results for P were above the DQO for RPD. There did not appear to be a trend between RPD and concentration for P, but most concentrations were < 10×MDL (Fig. 6). The %Recovery results of LFM analyses for all analytes were within DQOs for %Recovery. Although K results were within acceptable limits, it was of interest that %Recovery was consistently < 100% (one value > 100%) (Fig. 7). As with the QC results from ICP-MS analysis, meeting DQOs was most challenging at low (< 10×MDL) concentrations. At higher concentrations, the results presented here indicate that the method and instrument are performing within DQOs.

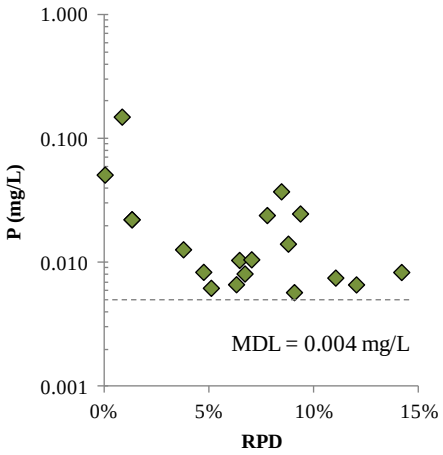


Figure 6. Control chart for selected Dup P analyses by ICP-OES showing a relationship between RPD and concentration.

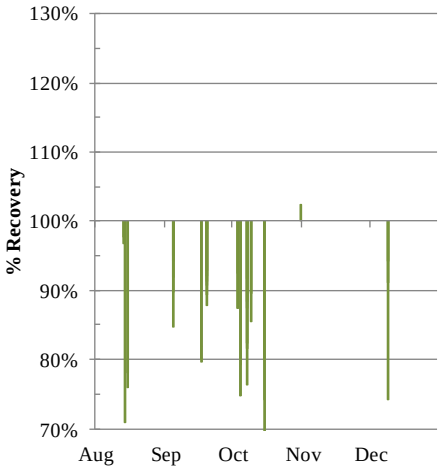


Figure 7. Control chart for selected %Recovery for K analyses by ICP-OES showing the relatively low recovery of K in LFM solutions.

Table 8: Results of QC analyses by ICP-OES and DQOs for elements of interest.

ICP-OES	Ca	Mg	Na	K	DQO
MDL	0.019 mg/L	0.004 mg/L	0.003 mg/L	0.0009 mg/L	To be determined by laboratory/study
Dup	x_m RPD = 1.16% SD = 0.957% MU = 0.299% n = 41; outliers = 0	x_m RPD = 0.670% SD = 1.33% MU = 0.415% n = 41; outliers = 0	x_m RPD = 1.10% SD = 3.33% MU = 0.107% n = 39; outliers = 2	x_m RPD = 1.25% SD = 3.17% MU = 0.989% n = 41; outliers = 3	RPD < 15% 2 outliers in 20 analyses
BDup	x_m RPD = 3.40% SD = 3.82% n = 20	x_m RPD = 1.96% SD = 1.86% n = 20	x_m RPD = 2.53% SD = 1.63% n = 20	x_m RPD = 2.22% SD = 1.51% n = 20	Same as Dup
High CCS	x_m %D = 1.59% SD = 1.44% n = 58; outliers = 0 Bias: negative	x_m %D = 3.68% SD = 1.62% n = 58; outliers = 0 Bias: positive	x_m %D = 3.12% SD = 2.69% n = 57; outliers = 0 Bias: negative	x_m %D = 5.29% SD = 2.68% n = 58; outliers = 2 Bias: negative	%D < 15% 2 outliers in 20 analyses
Low CCS	x_m %D = 2.49% SD = 1.47% n = 58; outliers = 0 Bias: negative	x_m %D = 1.87% SD = 1.45% n = 58; outliers = 0 Bias: positive	x_m %D = 3.68% SD = 2.84% n = 57; outliers = 2 Bias: negative	x_m %D = 5.89% SD = 2.80% n = 36; outliers = 1 Bias: positive	Same as High CCS
LFM	x_m %Recovery = 94.1% SD = 6.40% n = 42; outliers = 0	x_m %Recovery = 92.7% SD = 6.35% n = 51; outliers = 0	x_m %Recovery = 94.2% SD = 5.86% n = 58; outliers = 0	x_m %Recovery = 86.4% SD = 7.74% n = 66; outliers = 1	%Recovery 70–130% 2 outliers in 20 analyses

Table 8: (continued).

ICP-OES	P	S	Se	Cd	As
MDL	0.004 mg/L	0.018 mg/L	0.004 mg/L	0.0003 mg/L	0.004 mg/L
Dup	x_m RPD = 8.45% SD = 16.4% MU = 6.83% n = 23; outliers = 1	x_m |%RPD = 0.701% SD = 1.42% MU = 0.444% n = 41; outliers = 0	x_m RPD = 2.37% SD = 6.54% MU = 2.15% n = 37; outliers = 0	x_m RPD = 2.38% SD = 6.17% MU = 3.90% n = 10; outliers = n.a.	n.a.
BDup	x_m RPD = 23.8% SD = 26.5% n = 18 (n = 16 < 10×MDL)	x_m %RPD = 2.63% SD = 2.71% n = 20	x_m RPD = 7.83% SD = 8.27% n = 19	x_m %RPD = n.a. SD = n.a. n = 1	n.a.
High CCS	x_m %D = 3.12% SD = 1.98% n = 58; outliers = 0 Bias: negative	x_m %D = 2.39% SD = 1.73% n = 58; outliers = 0 Bias: negative	x_m %D = 2.56% SD = 1.72% n = 58; outliers = 0 Bias: negative	x_m %D = 3.72% SD = 2.08% n = 58; outliers = 0 Bias: negative	x_m %D = 3.79% SD = 1.39% n = 58; outliers = 0 Bias: negative
Low CCS	x_m %D = 4.79% SD = 2.49% n = 58; outliers = 0 Bias: negative	x_m %D = 2.85% SD = 2.01% n = 58; outliers = 0 Bias: negative	x_m %D = 3.71% SD = 1.92% n = 58; outliers = 0 Bias: negative	x_m %D = 4.14% SD = 1.95% n = 58; outliers = 0 Bias: negative	x_m %D = 4.80% SD = 2.10% n = 58; outliers = 0 Bias: negative
LFM	x_m %Recovery = 101% SD = 5.08% n = 67; outliers = 0	x_m %Recovery = 97.3% SD = 8.56% n = 46; outliers = 0	x_m %Recovery = 101% SD = 7.31% n = 52; outliers = 0	x_m %Recovery = 96.8% SD = 5.03% n = 67; outliers = 0	x_m %Recovery = 99.1% SD = 8.23% n = 67; outliers = 0

4.3 ICS

Analyses were conducted according to the SOP for analysis of common inorganic anions by ICS described in Chapter 3. Although NO_2, Br, and PO_4 can be analyzed by this method, results are not presented because sample concentrations were below MDLs. Acceptable limits for RPD were taken from EPA Method 300.1 (Hautman, 1997) and acceptable limits for outliers from (Konieczka & Namieśnik, 2009). These limits were adapted as DQOs for total elemental analysis by ICS in this laboratory.

The initial demonstration of laboratory performance for ICS was the same as for ICP-OES. Statistics including RPD, %D, x_m, SD, MU (based on Dup), %Recovery, and number of outliers are presented for all elements of interest (Table 10). As with ICP-MS and ICP-OES results, only select plots are presented for example purposes and all other plots can be found in Appendix A. The LDR and MDL for all analytes measured by ICS were determined and are presented in Table 9.

Table 9: ICS LDR and MDL for common inorganic anions.

	F mg/L	**Cl** mg/L	**NO_2** mg/L N	**Br** mg/L	**NO_3** mg/L N	**PO_4** mg/L PO_4	**SO_4** mg/L SO_4
MDL	0.05	0.05	0.05	0.2	0.03	0.05	0.05
Low LDR	MDL–4.0	MDL–65	MDL–3.2	MDL–8.2	MDL–16	MDL–3.2	MDL–65
High LDR	4.0–18	65–360	3.2–20	8.2–45	16–92	3.2–18	65–360

The MUs for the analytes of interest were all < 0.30% at the 95% confidence interval. The results of CCS analyses by ICS for Cl, NO_3, and SO_4 were within DQOs for %D. Low concentration CCS results (4.5 mg/L) for SO_4 had more outliers than acceptable, although the mean %D was within acceptable limits. It was determined that the integration parameters during peak area calculations were not optimized to deal with interference from the nearby PO_4 peak. Modifications to the SOP have been undertaken and an initial demonstration of laboratory performance is currently being evaluated. The results of Dup analyses for Cl, NO_3, and SO_4 were also within DQOs for RPD. Dup results for Cl and NO_3 had more outliers than acceptable but most were < 10×MDL, a range in which analytical error is greater. The results of BDup analyses for NO_3 and SO_4 were within DQOs and the results for Cl were above acceptable limits for RPD

(Fig. 8). It was suspected that contamination from algal growth as a result of unfiltered BDup samples may have interfered with Cl quantification; a peak with a similar retention time was identified. The results of LFM analyses for Cl, NO_3, and SO_4 were within DQOs for %Recovery. As with the QC results from ICP-MS and ICP-OES analyses, meeting DQOs was most challenging at low (< 10×MDL) concentrations. At higher concentrations, the results presented here indicate that the method and instrument are performing within DQOs.

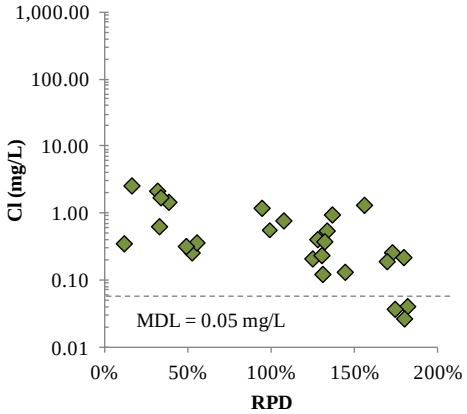


Figure 8. Control chart for selected BDup Cl analyses by ICS showing high RPD.

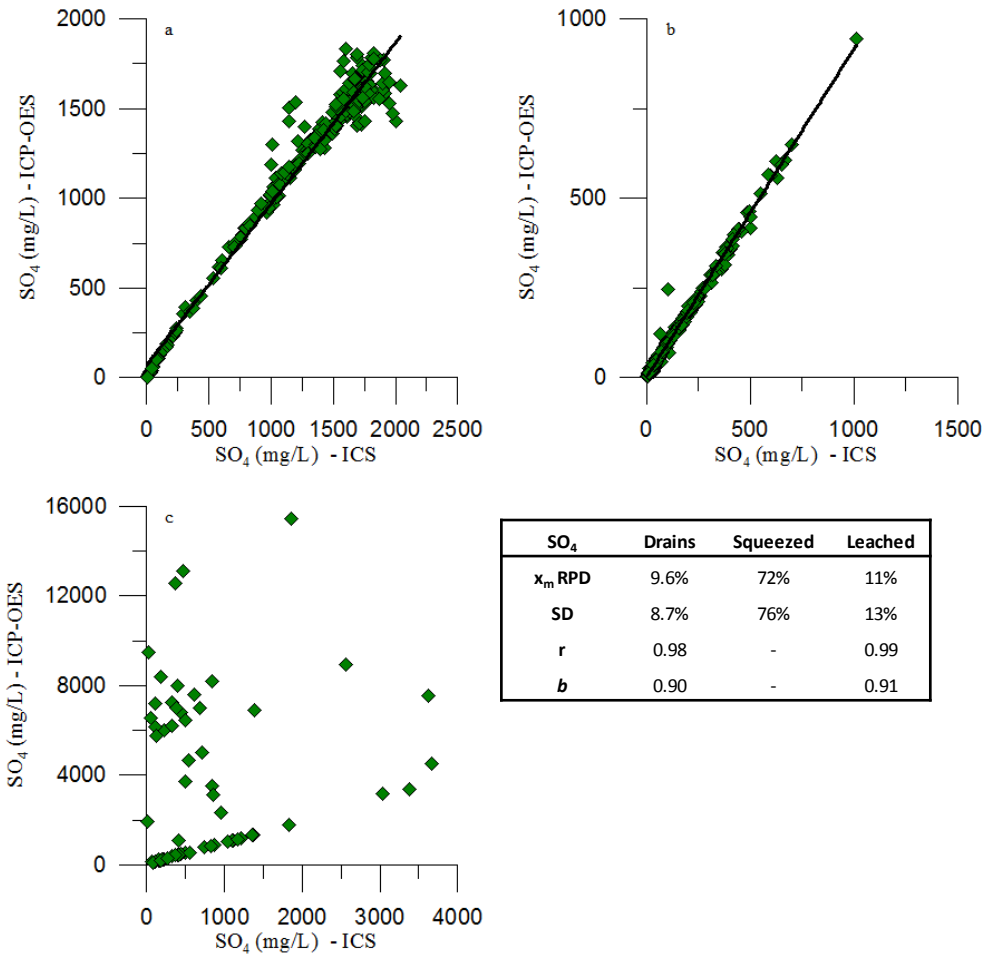
Table 10: Results of QC analyses by ICS and DQOs for elements of interest.

ICS	Cl	NO_3	SO_4	DQO
MDL	0.05 mg/L	0.03 mg/L	0.05 mg/L	To be determined by laboratory/study
Dup	x_m RPD = 1.9% SD = 1.5% MU = 0.28% n = 111; outliers = 4	x_m RPD = 1.5% SD = 1.5% MU = 0.30% n = 102; outliers = 9	x_m RPD = 0.81% SD = 1.1% MU = 0.21% n = 114; outliers = 8	RPD by Concentration: MDL–10×MDL: < 20% >10×MDL: < 10% 2 outliers in 20 analyses
BDup	x_m RPD = 107% SD = 57% n = 24	x_m RPD = 1.4% SD = 1.4% n = 27	x_m RPD = 1.9% SD = 2.1% n = 28	Same as Dup
High CCS	x_m %D = 1.3% SD = 0.73% n = 150; outliers = 0 Bias: positive	x_m %D = 2.6% SD = 1.5% n = 150; outliers = 4 Bias: positive	x_m %D = 2.5% SD = 1.6% n = 150; outliers = 7 Bias: positive	%D < 15% 2 outliers in 20 analyses
Low CCS	x_m %D = 2.2% SD = 1.3% n = 147; outliers = 3 Bias: positive	x_m %D = 2.1% SD = 1.4% n = 147; outliers = 6 Bias: positive	x_m %D = 7.0% SD = 5.0% n = 125; outliers = 21 Bias: positive	Same as High CCS
LFM	x_m %Recovery = 97% SD = 4.2% n = 162; outliers = 1	x_m %Recovery = 94% SD = 4.9% n = 139; outliers = 1	x_m %Recovery = 89% SD = 6.8% n = 81; outliers = 3	%Recovery = 85–115%

4.4 Intra-Lab Comparisons

Analytical results from different methods were compared to evaluate the quality of data produced by each method. Comparisons could only be made between common analytes. Comparisons between ICS and ICP-OES results were undertaken for S (SO_4 by ICS and S by ICP-OES). Comparisons between ICP-MS and ICP-OES results were undertaken for Ca, Mg, K, Na, P, Se, and Cd. DQOs were set at < 15% RPD, which is the EPA acceptable limit for CCS results. Data were compiled from the analysis of sample types collected from (1) rock drains; (2) mechanical squeezing of core samples; and (3) aqueous leaching of core samples. The sum of average major and trace ions concentrations (SO_4, Ca, Mg, Na, K, P, Se, As, Cd) varied between the three types of samples. The sum was calculated by adding the average concentration of each analyte for the samples compared in this section. Maximum and minimum sums were calculated by separating averages depending on which method resulted in higher or lower average concentration. An exception for SO_4 was made due to the large scatter in the data (see below) with only the concentrations that correlated being averaged. Rock drains had the highest average ion sum (1796–1917 mg/L), mechanical squeezing had a mid- range ion sum (430–1184 mg/L), and leached samples had the lowest ion sum (141–154 mg/L). High ion sums may introduce error due to matrix interference or by the higher dilution required, and therefore increased potential error.

A comparison was made between SO_4 analyzed by ICS and S (calculated back to SO_4) by ICP-OES for the three sample types (Fig. 9). The SO_4 results from drain and leached samples showed strong linear relationships with *b* values close to 1, indicating good agreement between the methods across the range of concentrations encountered. The SO_4 results from squeezed samples were more complex. The mean RPD was high and, as a whole population, there did not appear to be a relationship between the methods. Some results did correlate and had a strong relationship (R^2 = 0.98) with a *b* value of 1.1. These samples suggest a source of S other than SO_4 was reported by the total S analysis by ICP-OES. For example, S_2O_3 is often formed from pyrite oxidation (Nordstrom, 2000). This trend appeared to be unique to the squeezed samples, which did have pyrite in the squeezed core. The excellent agreement between some squeezed samples and not others may indicate that the complex nature of the samples is the source of the discrepancy rather than analytical error. DQOs were met for the drain and leached samples, but not for squeezed samples.

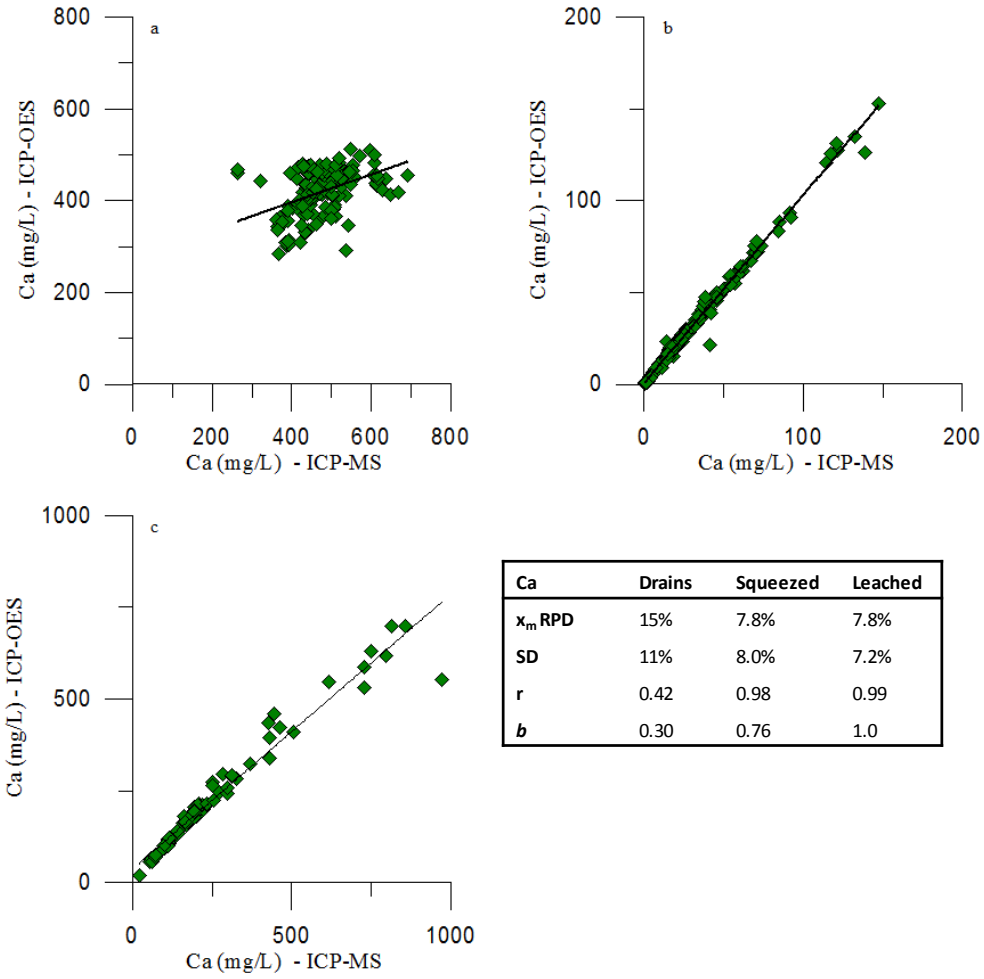


SO_4	Drains	Squeezed	Leached
x_m RPD	9.6%	72%	11%
SD	8.7%	76%	13%
r	0.98	-	0.99
b	0.90	-	0.91

Figure 9. Comparison of SO_4 results from ICS and ICP-OES for a) drains, b) leached, and c) squeezed samples.

The agreement for Ca results from ICP-MS and ICP-OES differed for the three sample types (Fig. 10). Drain samples had a weak and fairly scattered relationship between methods. This scatter is reveal in drain samples results for Ca, Mg, K, P, Se, and Cd and somewhat in Na. It was suspected that TDS or high calcite concentrations were the source of the scatter in the drain samples because they had the most complex matrix. An investigation into the effect of TDS showed little difference in RPD or %D (data not shown here). The pH of the preserved samples was also verified, and no difference was found between the types of samples and alkalinity was not higher in the drain samples either. Regardless of the scatter, the drain results fell within DQOs. Leached and squeezed samples showed strong linear relationships, indicating good agreement between the methods. Results by ICP-OES were generally lower than by ICP-MS in the squeezed samples. This is unexpected considering the bias of CCS results for ICP-OES was

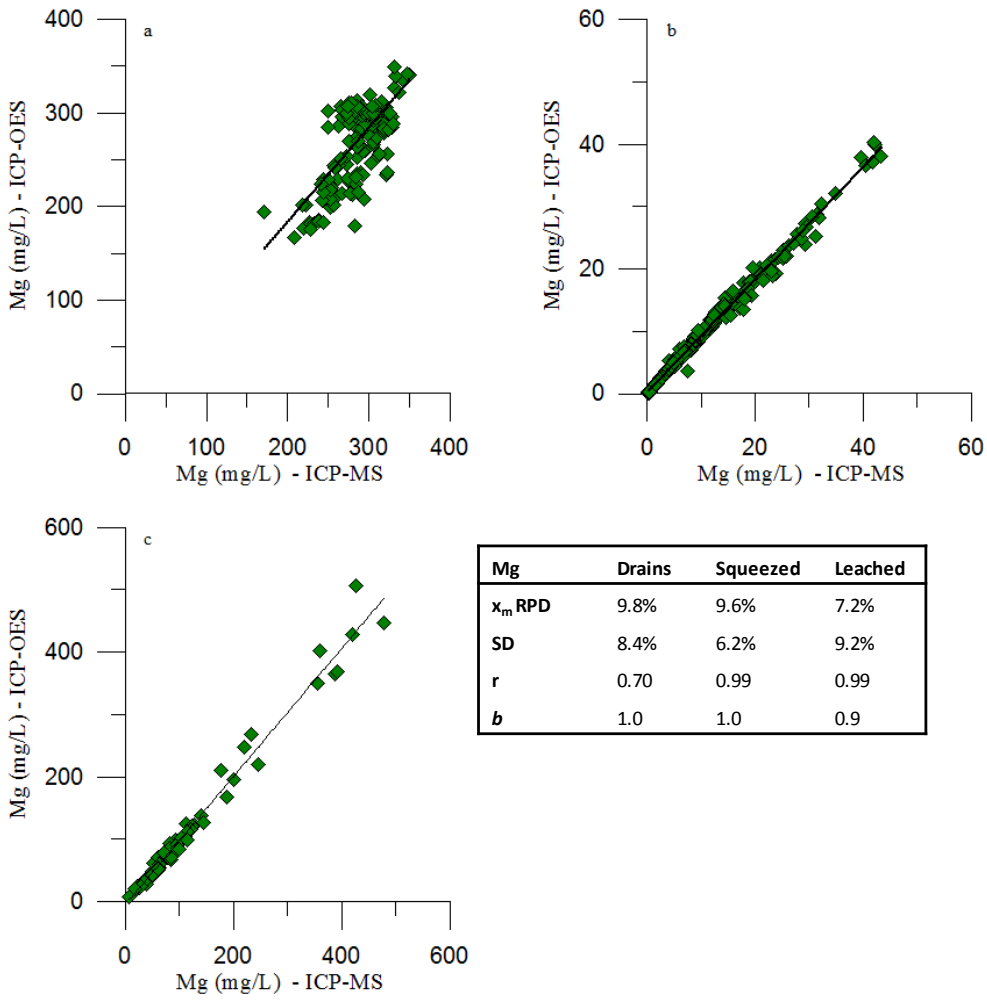
negative (measured > true value) and for ICP-MS was positive (measured < true) for Ca, although the biases were within acceptable limits for both methods.



Ca	Drains	Squeezed	Leached
x_m RPD	15%	7.8%	7.8%
SD	11%	8.0%	7.2%
r	0.42	0.98	0.99
b	0.30	0.76	1.0

Figure 10. Comparison of Ca results from ICP-MS and ICP-OES for a) drains, b) leached, and c) squeezed samples.

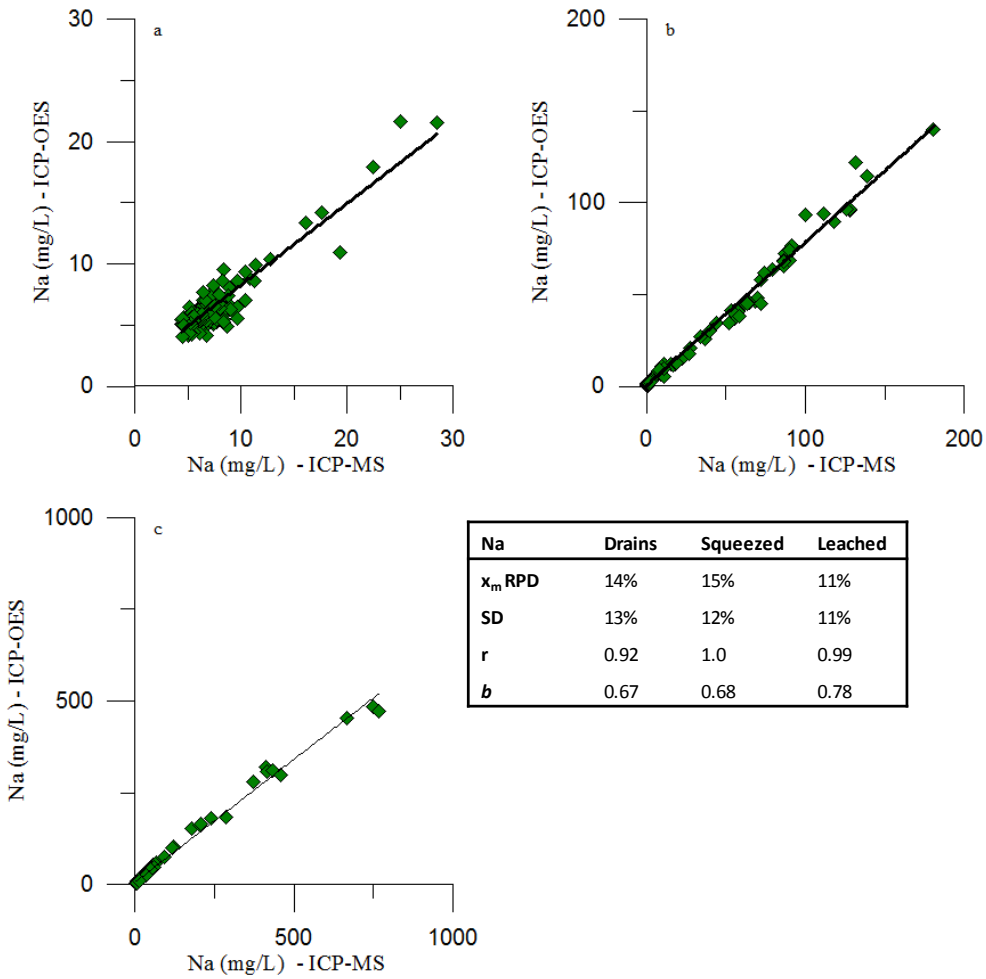
The agreement for Mg results from ICP-MS and ICP-OES analyses also differed for the three sample types (Fig. 11). Drain samples showed a scattered, moderately strong linear relationship with a *b* value of 1.0. This trend indicates that the fair amount of scatter observed in the data was randomly distributed and not systematic. Squeezed and leached samples showed a strong linear relationship with *b* values close to 1.0, indicating good agreement between the methods. Results by ICP-OES for leached samples generally had lower concentrations than results by ICP-MS, although all results were within DQOs.



Mg	Drains	Squeezed	Leached
x_m RPD	9.8%	9.6%	7.2%
SD	8.4%	6.2%	9.2%
r	0.70	0.99	0.99
b	1.0	1.0	0.9

Figure 11. Comparison of Mg results from ICP-MS and ICP-OES for a) drains, b) leached, and c) squeezed samples.

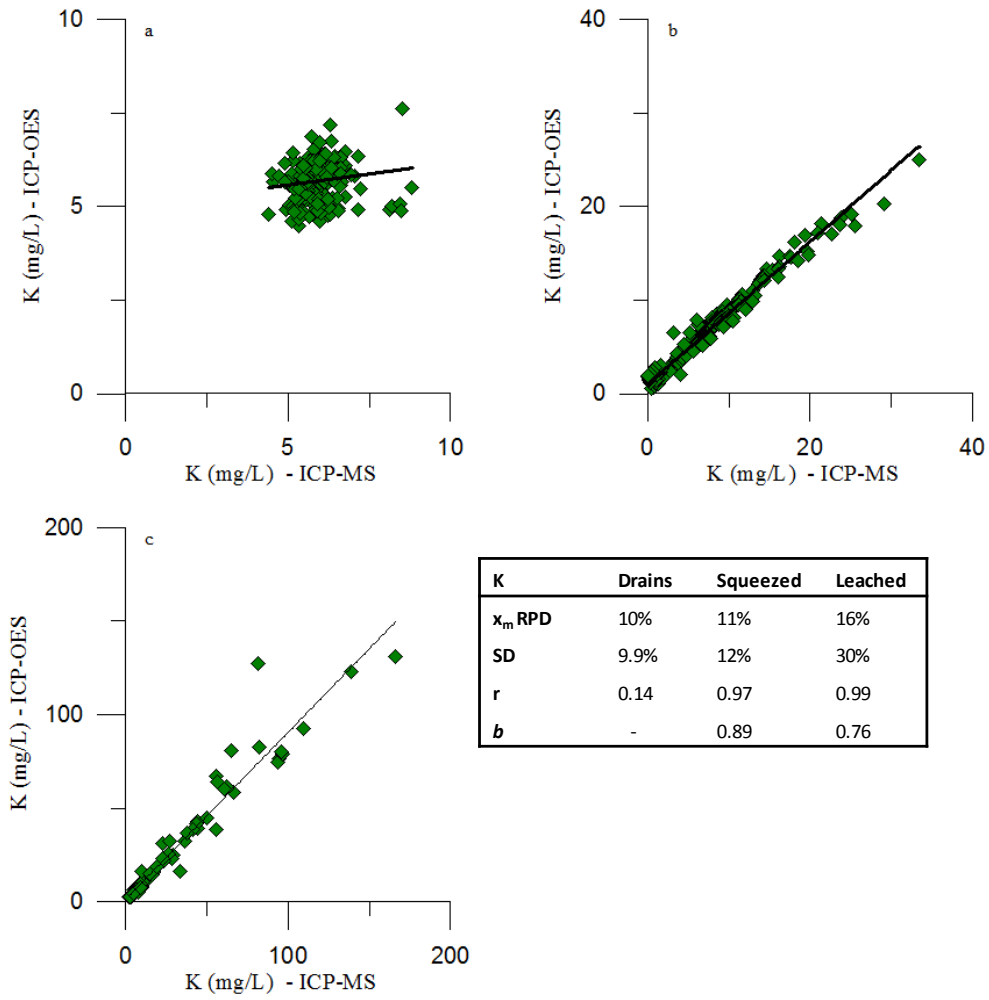
There was good agreement for Na results by ICP-MS and ICP-OES for the three types of samples (Fig. 12). Drain, squeezed, and leached samples all showed strong linear relationships with *b* values < 1.0. This indicates good agreement between the methods across the concentration range encountered. Although ICP-OES data reported were somewhat lower than ICP-MS data for all three sample types, the results were still within DQOs.



Na	Drains	Squeezed	Leached
x_m RPD	14%	15%	11%
SD	13%	12%	11%
r	0.92	1.0	0.99
b	0.67	0.68	0.78

Figure 12. Comparison of Na results from ICP-MS and ICP-OES for a) drains, b) leached, and c) squeezed samples.

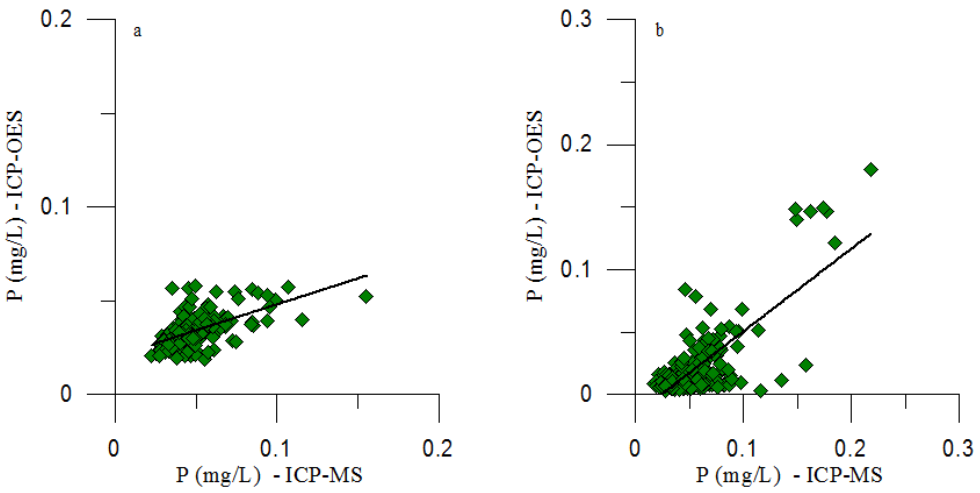
The agreement for K results from ICP-MS and ICP-OES analyses differed for the three sample types (Fig. 13). Drain samples again showed no relationship between ICP-MS and ICP-OES results, which may indicate matrix interference unique to the drain samples similar to Ca and Mg results. Even with this scatter, drain result RPD values did fall within DQOs, but the lack of correlation between the two methods was of concern. Squeezed samples showed a strong linear relationship with a *b* value close to 1.0, indicating good agreement between the methods across the range of concentrations encountered. Leached samples also showed a strong linear relationship with a *b* value close to 1.0, although the RPD was not within DQOs. ICP-OES data reported somewhat lower values than ICP-MS for all three sample types.



K	Drains	Squeezed	Leached
x_m RPD	10%	11%	16%
SD	9.9%	12%	30%
r	0.14	0.97	0.99
b	-	0.89	0.76

Figure 13. Comparison of K results from ICP-MS and ICP-OES for a) drains, b) leached, and c) squeezed samples.

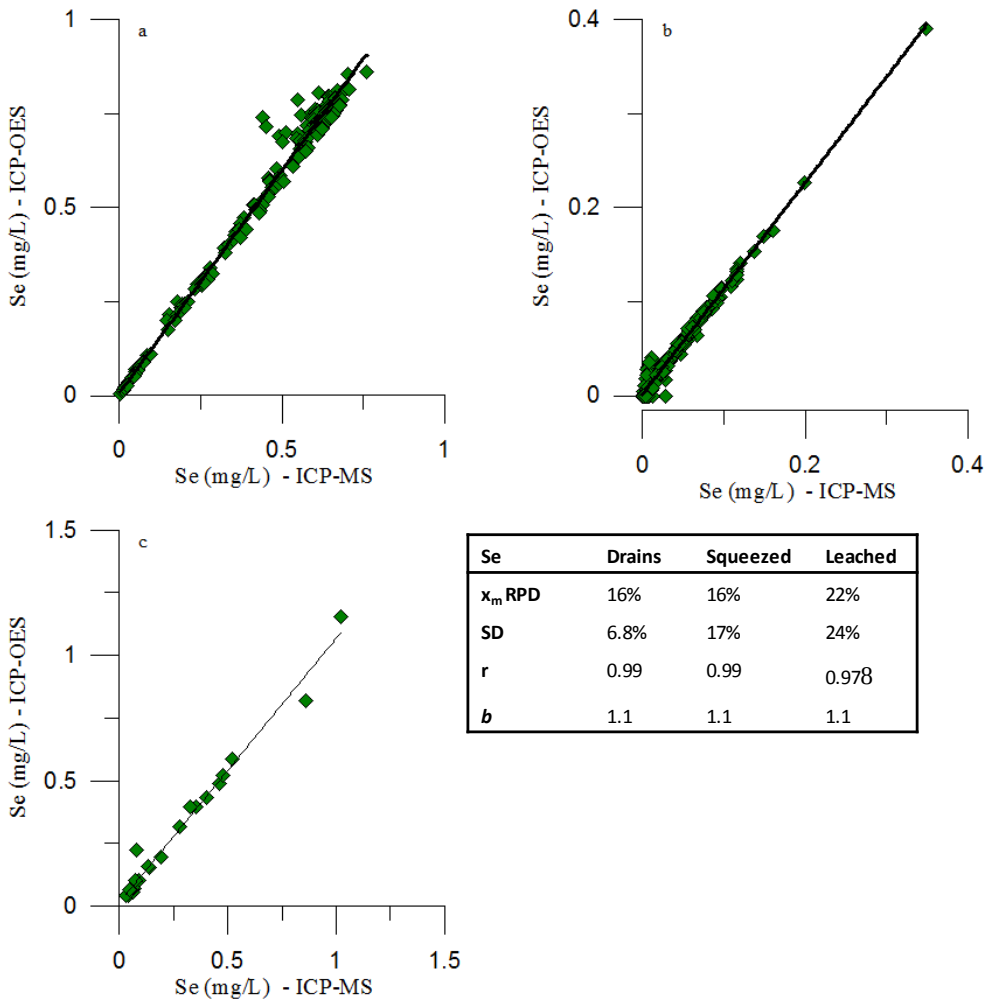
The comparison of P results from ICP-MS and ICP-OES analyses could only be made for drain and leached samples (Fig. 14). Squeezed samples analyzed by ICP-OES were below the P MDL after dilution to required volume and no values could be compared. There was poor agreement between the methods for the drain and leached samples. ICP-OES data generally had lower concentrations than ICP-MS data. The majority of results were < 10×MDL of the ICP-OES, which may explain the discrepancy of results between the two methods. Phosphorus results did not meet DQOs.



P	Drains	Squeezed	Leached
x_m RPD	34%	-	107%
SD	23%	-	40%
r	0.57	-	0.75
b	0.28.	-	0.66

Figure 14. Comparison of P results from ICP-MS and ICP-OES for a) drains and b) leached samples.

The comparison of Se results from ICP-MS and ICP-OES analyses (Fig. 15) for all three sample types had high RPD values and did not meet DQOs. Even with high RPD values, the relationships between methods for all sample types were strong with *b* values close to 1.0. All three trends showed ICP-OES data reporting somewhat higher than ICP-MS, which was expected considering the bias for CCS results for ICP-OES was negative (measured > true) and for ICP-MS was positive (measured < true). Most of the ICP-OES results were < 10×MDL, which may explain the high RPD but strong linear correlation between methods.

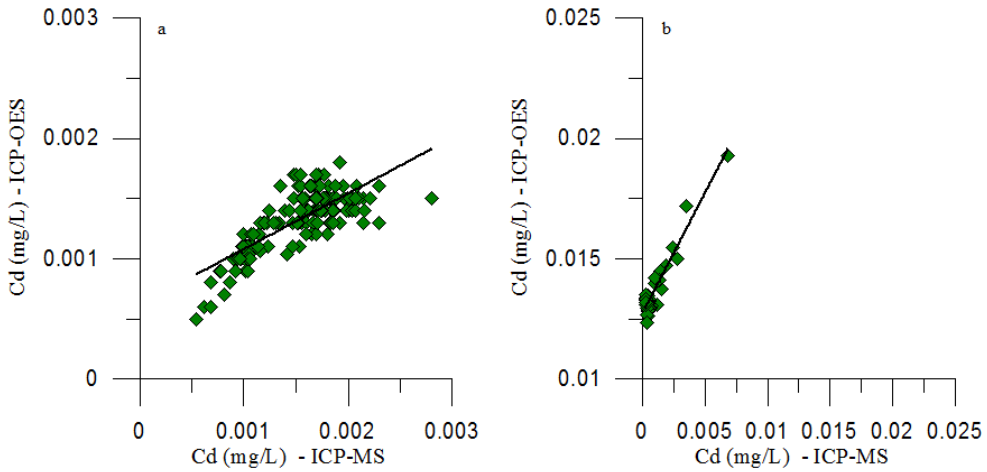


Se	Drains	Squeezed	Leached
x_m RPD	16%	16%	22%
SD	6.8%	17%	24%
r	0.99	0.99	0.978
b	1.1	1.1	1.1

Figure 15. Comparison of Se results from ICP-MS and ICP-OES for a) drains, b) leached, and c) squeezed samples.

The comparison of Cd results from ICP-MS and ICP-OES analyses could only be made for drain and squeezed samples (Fig. 16). Leach samples analyzed by ICP-OES were below the Cd MDL and no values could be compared. Agreement between methods for both drain and squeezed samples did not meet DQOs, especially for squeezed samples. The drain samples showed a scattered relationship between methods. The low *b* values indicated some agreement between the methods across most of the range of concentrations encountered, but ICP-OES data generally reported lower than ICP-MS data. Results from squeezed samples were more complex, with a strong linear relationship and a *b* value of 1.0, which should indicate good agreement between the methods. However, the high RPD between methods and a high y-intercept revealed

an offset between the methods, indicating poor agreement. Concentrations were < 10×MDL of the ICP-OES and likely the source of the discrepancy between results from the two methods.



Cd	Drains	Squeezed	Leached
x_m RPD	16%	188%	-
SD	12%	17%	-
r	0.77	0.93	-
b	0.46	1.0	-

Figure 16. Comparison of Cd results from ICP-MS and ICP-OES for a) drains and b) leached.

In summary, agreement between the methods across all analytes was better at higher concentrations and began to deviate at low (< 10×MDL) concentrations, especially for trace metals. An interesting exception was SO_4 in the squeezed samples, which displayed two populations: one falling along a straight line and another scattered above the line. This suggested an additional source of S in the squeezed water. The majority of P and Cd concentrations were < 10×MDL of the ICP-OES, and therefore these low concentrations were likely the source of the discrepancies between the two methods. ICP-OES generally reported similar or lower concentrations compared to ICP-MS with respect to the analytes compared here. An exception was Se, in which ICP-OES reported similar or somewhat higher concentrations compared to ICP-MS. The effects of leverage points on the trend lines requires further investigation.

As another check on the quality of the water data, the mean CBE was calculated for the drain and squeezed samples. CBE could not be calculated for the leached samples because alkalinity was not measured in these samples. Laboratory alkalinity was measured by titration

using the analytical procedure in EPA 310.1 with a Radiometric Titralab Tim870 Titration Manager Autoburette coupled to a TIM800 TitraLab Titration Manager, TimTalk 8 software, and a titrant concentration of ~ 0.1 M HCl. For calculation of CBE, Cl, NO3, and SO4 were measured by ICS and alkalinity (as mg/L $CaCO_3$) by titration and Ca, Mg, Na, and K were measured by ICP-OES. In a few cases, alkalinity was measured on drain samples in the field. The mean difference in CBE calculated using alkalinity measured in the field or laboratory differed by < 1% (0.78% ± 0.93%; n = 18) even though the alkalinity measurements themselves differed by a mean of 16% (±18%) with field measurements reporting higher concentrations in 16 of 18 measurements. The mean CBE for drain samples was 6.76% (±3.38%) 130 positive results in a total of 133 indicating an excess of cations or deficiency of anions. The mean CBE for squeezed samples was 0.640% (±3.08%; n = 12) with and even distribution between positive and negative results. The typical criteria for acceptance of water samples with similar concentration ranges are 5%. Three samples submitted to ALS had a mean CBE of 4% with all results positive. Although three samples is too few to make any firm judgement, it does suggest that there may be an anion not accounted for in these analyses.

4.5 Inter-Lab Comparisons

Analytical results from different methods and laboratories were compared to evaluate the quality of data produced by each laboratory and method. Analytes reported by the SRC included Ca, Mg, K, Na, Se, Ar, Cd, and S analyzed by ICP-MS. Results from P analysis reported by SRC were below or at MDLs and were not reported here. Analytes reported by ALS included Ca, Mg, and K by ICP-MS. Comparisons between SRC, U of S ICP-MS, and U of S ICP-OES as well as between ALS, U of S ICP-MS, and U of S ICP-OES were undertaken for Ca, Mg, K, and Na. Comparisons between SRC, U of S ICP-MS, and ICP-OES were only reported for Se (and not As and Cd). U of S ICP-OES results for As and Cd were below MDLs and therefore comparisons were only made between SRC and U of S ICP-MS for As and Cd. Comparisons between SRC, U of S ICP-OES, and ICS were made for S. The number of results was too few for statistical analysis, but general trends are investigated. Figures can be found in Appendix A.

The results for Ca, Mg, Na, K, S, and Se showed good agreement between methods and laboratories. In one sample, U of S ICP-MS consistently reported lower cation concentrations than the other methods, but more comparisons must be made to determine the source of the discrepancy. The results for As appeared to vary between SRC and U of S ICP-MS, with SRC

reporting an order of magnitude lower. As concentrations were < 10× the SRC MDL and this was likely the source of the discrepancy. Therefore, the agreement between methods cannot be determined at this time. The results for Cd also appeared to vary, with SRC reporting high for all except one result. Again, concentrations were < 10× the SRC MDL and this was likely the source of the discrepancy. Therefore, the agreement between methods for Cd cannot be determined at this time.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

The complex nature of water samples collected from diverse geologic media creates analytical challenges with respect to the measurement of both major ions and trace metals. Such challenges include small sample volumes, alteration of samples during collection, transportation, storage, and pretreatment (Paschke, 2003), matrix interference (Singh et al., 1996; Becker and Dietze, 1998; Lopez-Rutz, 2000; Hoenig, 2001; Salomon et al., 2001), and wide ranges of concentrations of individual analytes as well as orders of magnitude differences between major and minor analytes (Singh et al., 1996; Lopez-Rutz, 2000). A formal QCP provides the foundation necessary to overcome these challenges and ensure the data generated by the analytical laboratory are of requisite quality (Ibe and Kullenberg, 1995; Field Sampling Manual, 2003; Taverniers et al., 2004; Hoskins, 2009; Olivares and Lopes, 2012).

The objectives of this thesis were to: (1) develop a QCP for aqueous samples that includes SOPs and QC protocols to provide a foundation for producing high quality results; (2) investigate and document the quality of the data produced by the NSERC-IRC Aqueous and Environmental Geochemistry Laboratory in 2013; and (3) make recommendations to optimize the ongoing production of high quality and reliable data where appropriate.

A QCP was developed and implemented in the Aqueous and Environmental Geochemistry Laboratory to ensure standardization of methods, document uncertainty, and reinforce confidence in the quality of the data produced. As part of the QCP, a unique QCM was drafted based on foundational guidelines for data generation and the requirements of the laboratory and the research it supports. The QCM documents all of the resources, policies, and procedures that may have bearing on the quality of the data. Improvements to the original SOPs were made while drafting of the QCM. Further improvements will be implemented following the evaluation of the QC data in this document.

The data produced by the laboratories during 2013 met the standards for high quality results required by DQOs in most cases. Increases in RPD for Dup and %D for CCSs occurred as concentrations approach the MDLs of P, Se, Cd, and As. The %D and RPD values at concentrations near (~10×) the levels set by the Water Quality Guideline for the Protection of Aquatic Life (0.005 mg/L for As and 0.001 mg/L for Cd and Se) (Canadian Council of Ministers

of the Environment, 2014) were within acceptable limits (< 25%; Table 11). Therefore, the quality of the data meets to standards required for the research in which it is employed.

Several QC solutions were analyzed by each analytical method (ICP-MS, ICP-OES, and ICS) and statistical analyses of the results were used to calculate variability and bias from sample handling and analysis and the MUs that should be used when reporting data. Also, a table of method performance for each analyte was constructed (Table 11) detailing method options and concentration ranges. The recommended method (shaded) is based on the quality of the data as well as analytical cost. Evaluation of the data generated by the laboratory was used to determine if the QCP was performing according to DQOs. The DQOs selected were the limits of acceptability from corresponding EPA methods. Where DQOs were not met, recommendations were made to improve data quality.

Table 11. Method performance for selected analytes based on Dup and CCS evaluations. Good performance has %D and RPD ranges of 0–15% and Fair has %D and RPD ranges of 15–25% and recommended method shaded in green.

Analyte	ICP-MS	ICP-OES	ICS
Cl	n.a.	n.a.	Good > 0.2 mg/L Fair 0.1–0.2 mg/L Poor 0.05–0.1 mg/L
NO_3	n.a.	n.a.	Good > 0.1 mg/L Poor 0.05–0.1 mg/L
SO_4 / S	n.a.	Good	Good
Ca	Good	Good	n.a.
Mg	Good	Good	n.a.
Na	Good	Good	n.a.
K	Good	Good	n.a.
P	Good > 0.1 mg/L Fair 0.01–0.1 mg/L Poor < 0.01 mg/L	Good > 0.01 mg/L Fair 0.004–0.01 mg/L	n.a.
Ba	Good	n.a.	n.a.
Se	Good > 0.02 mg/L Fair 0.0005–0.02 mg/L	Good > 0.01 mg/L Fair 0.004–0.01 mg/L	n.a.
Cd	Good > 0.001 mg/L Fair 0.0002–0.001 mg/L Poor < 0.0002 mg/L	Good > 0.001 mg/L Fair 0.0006–0.001 mg/L Poor < 0.0006 mg/L	n.a.
As	Good > 0.03 mg/L Fair 0.004–0.03 mg/L Poor < 0.004 mg/L	Good > 0.05 mg/L Fair 0.004–0.05 mg/L	n.a.

The biases of the analytical methods were evaluated for each analyte using CCS solutions. Most of the analytes measured in CCS solutions by ICP-MS (Ca, Mg, Ba, Se, Cd, As) had a small but persistent positive bias, indicating that the reported results were lower than true values. Na and P both had a small negative bias. High concentrations of K produced a small but persistent negative bias. With the exception of Na, P, and K, results generally have a positive bias and therefore indicate that recovery of the analytes is not complete but within acceptable limits. In the case of Na and P, the bias is weak and therefore recovery is likely not a problem. In

the case of K, the persistent negative bias indicates an excessive recovery but within acceptable limits.

Bias evaluations for ICP-OES and ICS analyses were made from results of both CCS and LFM solutions. Most analytes measured in CCS solutions by ICP-OES (Ca, Na, K, S, P, Se, Cd, As) had a small persistent negative bias. Mg had a small persistent positive bias. Most of the analytes measured in LFM solutions (Ca, Mg, Na, K, S, Cd, As) had %Recoveries below 100% (86–99%), indicating incomplete recovery. P and Se had %Recoveries of 101%, indicating recovery is likely not a problem. Although all biases and recoveries were within acceptable limits, it is of interest to note that CCS results under-report concentrations while LFM over-report concentrations for most analytes (Ca, Na, K, S, Cd, As) and vice versa for Mg. All analytes measured by ICS (Cl, NO_3, SO_4) had positive biases and %Recoveries < 100% (88–97%), which indicated that the reported results were lower than the true values both in CCS and LFM solutions.

It is recommended that the biases for all methods continue to be monitored to determine if they increase with time or become erratic. A change in the magnitude or direction of the bias may indicate issues with the method or instrument. It would also be of value to determine the source of these biases, although this may be difficult. Analysis of blanks and LFM associated with each step in the procedure may indicate at which step the bias is introduced.

CCS solutions were also used to evaluate the performance of the methods and instruments. Most of the analytes measured in CCS solutions by ICP-MS (Ca, Na, K, Ba, Se, Cd) were within DQOs. Mg and As CCS results had a larger than acceptable number of outliers and, in both cases, the source of the outliers is unclear although the As outliers are likely related to interference and a relatively low degree of ionization. All of the analytes measured in CCS solutions by ICP-OES (Ca, Mg, Na, K, P, S, Se, Cd) were within DQOs. The CCS results from ICS for Cl and NO_3 were within DQOs but SO_4 results had a larger than acceptable number of outliers at low (4.5 mg/L) concentrations. It was determined that the integration parameters during peak area calculations were not optimized to deal with interference from the nearby PO_4 peak. Modifications to the SOP for SO_4 analysis by ICS were undertaken and an initial demonstration of laboratory performance is currently being conducted. It is recommended that the source large number of Mg and As outliers measured by ICP-MS be determined and an initial demonstration of laboratory performance be undertaken. It is also recommended that a low (<

1500 mg/L) P concentration CCS solution and/or a high (> 0.005 mg/L) Cd concentration CCS solution be introduced to routine ICP-MS analyses if sample concentrations fall into these ranges.

Precision evaluations were made using Dup and BDup. Most of the analytes measured in Dup by ICP-MS (Ca, Mg, Ba, Se, Cd, As) were within DQOs. The Na and K Dup results had a larger than acceptable number of outliers and, in both cases, the source of the outliers is unclear. P, Se, and As Dup results also had a larger than acceptable number of outliers that may be related to the MDL. Most of the analytes measured in BDup by ICP-MS (Ca, Mg, Na, K, Ba, Se) were within DQOs. The RPD results for P and As both appeared to have relationships with concentration, but a clear trend between concentration and RPD was not apparent for Cd results. Most of the analytes measured in Dup by ICP-OES (Ca, Mg, Na, K, Cd) were within DQOs. The P, Se, and As Dup results had a larger than acceptable number of outliers that may be related to the MDL. Most of the analytes measured in BDup by ICP-OES (Ca, Mg, Na, K, S, Se, Cd) were within DQOs. The RPD results for P appeared to have a relationship with concentration. All analytes measured in Dup by ICS (Cl, NO_3, SO_4) were within acceptable mean RPD but Cl and NO_3 results had a larger than acceptable number of outliers. Both Cl and NO_3 RPD results appeared to have a relationship with concentration. The NO_3 and SO_4 results in BDup by ICS were within acceptable DQOs. It is suspected that contamination from algal growth as a result of BDup samples not being filtered may interfere with Cl analysis. A peak with a similar retention time to Cl that may cause interference was identified. The SOP for BDup generation has been updated.

From the precision evaluation based on Dup and BDup results, it is recommended that the MDL concentrations for P, Se, and As measured by both ICP-MS and ICP-OES be re-evaluated. Based on these evaluations, it should be determined if this limit is the source of outliers and, if so, determine the acceptable error near the MDL. If the source of the outliers is not related to the MDL, it is recommended that the source of these outliers be determined systematically. Several laboratory fortified blanks (LFB) and LFM solutions with a range of concentrations should be analyzed and %Recovery calculated to determine any effect on the results. In the case of Cl measured by ICS in BDup, it is recommended that an investigation into the unknown peak and its effect on Cl be undertaken to determine if it interferes with Cl and if the high mean RPD is associated with algal contamination. If this is not the source of the high

error, it is recommended that the source be determined and an initial demonstration of laboratory performance be undertaken. The precision evaluation based on Dup was also used to estimate MUs based on a 95% confidence interval. All MUs estimated while evaluating Dup were < 5% and should be used when reporting data in the future.

In addition to the previously mentioned QC solutions, the fitness of each method was evaluated by the use of intra-laboratory comparisons of various methods that measure the same analytes. Three different groups of aqueous samples were analyzed: (1) drain samples, (2) squeezed samples; and (3) leached samples. SO_4 measured by ICS was compared to total S measured by ICP-OES. The agreement between data from drain and leached samples was within DQOs; however, approximately half of the squeezed samples had ICP-OES results exceeding ICS results while the other half had a strong linear relationship. It is suspected that the nature of the samples may be the source of the error (i.e., excess S as a form other than SO_4 measured by ICP-OES but not ICS), rather than analytical error. Ca, Mg, and K measured by ICP-MS and ICP-OES in the drain samples had poor agreement, while concentrations in squeezed and leached samples had agreement within DQOs. The source of the poor agreement in the drain sample data is unknown, although the complex chemistry of these samples is likely the source of error. Drain samples had the highest ion sums which would either introduce matrix interference or dilution error. K measured by ICP-MS and ICP-OES did have acceptable agreement, but there is a lack of relationship between methods. P measured by ICP-MS and ICP-OES had poor agreement, although the results were < 10×MDL of the ICP-OES and these low concentrations are likely the source. Se measured by ICP-MS and ICP-OES had strong linear relationships but RPD results above DQOs. Cd measured by ICP-MS and ICP-OES in drain and squeezed samples had weak agreement. It is suspected that the weak agreement of Se and Cd between the methods is related to the MDL.

From the comparison of different methods within the laboratory, it is recommended that the MDLs of P, Se, and Cd be re-evaluated in the same manner as the precision evaluation indicates. The source of the poor agreement of Ca, Mg, and K in the drain samples should also be investigated in the same manner as the precision evaluation indicates. It is also recommended that the source of the elevated S values be determined to ensure it is not analytical error.

From the comparison of different laboratories as well as different methods within the laboratory, agreement of analyte concentrations were excellent with the exception of deviations

near the MDL of each method for As and Cd. It is recommended that samples and LFB solutions continue to be submitted quarterly to external laboratories to evaluate the quality of the analytical laboratory.

Most of the DQOs set out by the QCP were met and confidence in the quality of the data produced in the laboratory was assured. In cases where DQOs were not met, the quality of the data is still sufficient for the nature of the studies the data is used for (i.e. water quality). Therefore, re-definition of DQOs is required as well as investigations into the source of the failure will be undertaken. This includes, but is not limited to, re-evaluation of MDLs, source of outliers, source discrepancy of SO_4 concentrations from ICS and ICP-OES and Ca, Mg, and K concentrations from ICP-MS and ICP-OES, and possible matrix interference. The identification of these strengths and weaknesses improved the laboratory methods and, as a result, has and will continue to increase the quality of the data produced.

The QCP implemented in the laboratory is the foundation upon which quality data has been and will continue to be produced. QC protocols will continue to be monitored and the QCP and QCM will be reviewed and revised when DQOs are not achieved or there are changes in laboratory staff, equipment, or the specific requirements of the studies the laboratory supports. A clear understand of DQOs by the laboratory staff will not only ensure current data production at the requisite quality, but also encourage innovation and improvement of data quality. The QCM will also provide an excellent training tool for new staff.

CHAPTER 6
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APPENDIX A – FIGURES

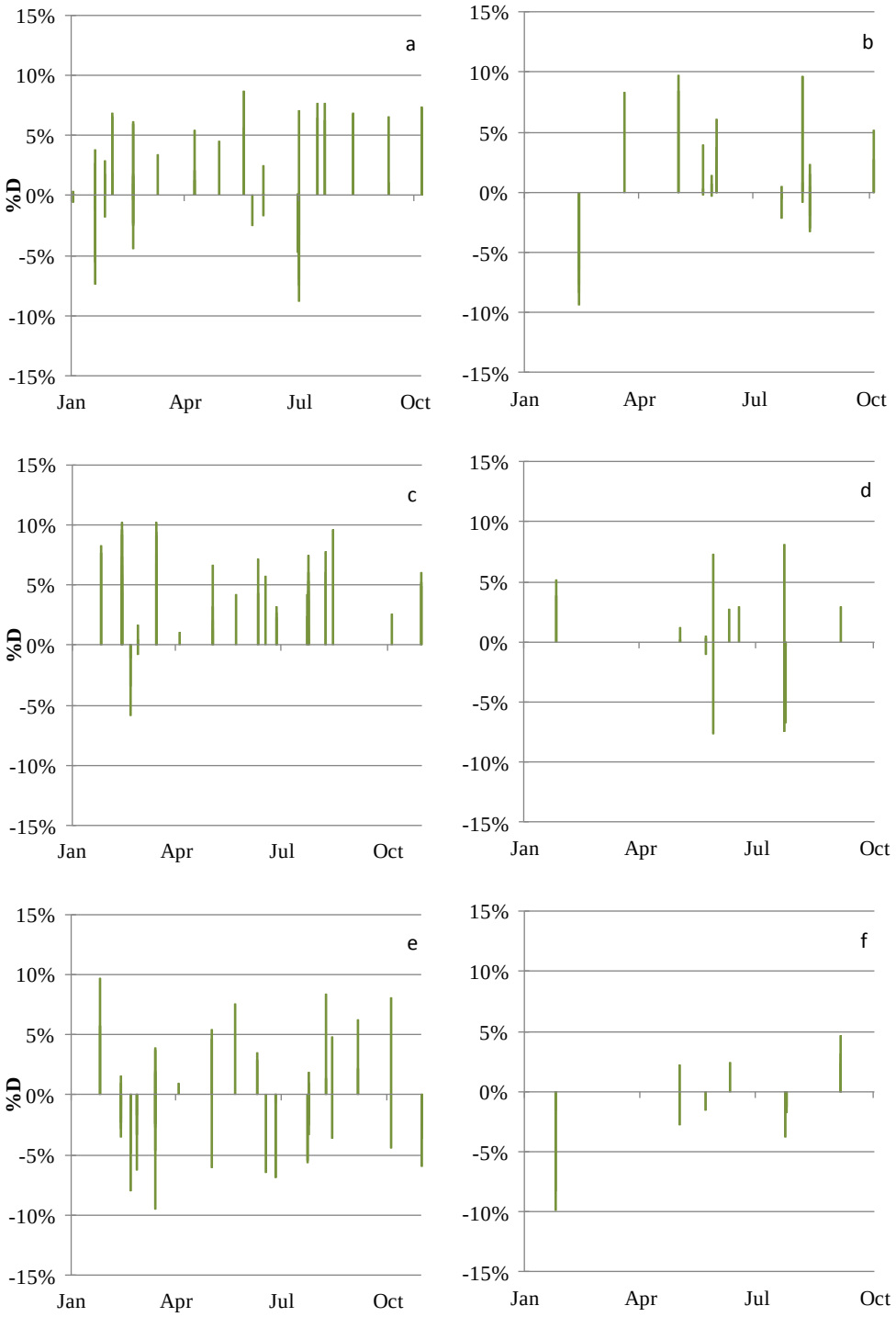

Figure A. Control charts for selected 2013 calibration control standards (CCS) for ICP-MS analyses: a) high concentration Ca CCS (~50 g/L), b) low concentration Ca CCS (~20 mg/L), c) high concentration Mg CCS (~22 g/L), d) low concentration Mg CCS (~10 mg/L), e) high concentration Na CCS (~50 g/L), and f) low concentration Na CCS (~20 mg/L).

Figure B. Control charts for selected 2013 calibration control standards (CCS) for ICP-MS analyses: a) high concentration K CCS (~15 g/L), b) low concentration K CCS (~0.3-0.7 mg/L), c) high concentration P CCS (~1500 mg/L), d) high concentration Ba CCS (~680 mg/L),and e) low concentration Ba CCS (~0.01-0.05g/L).

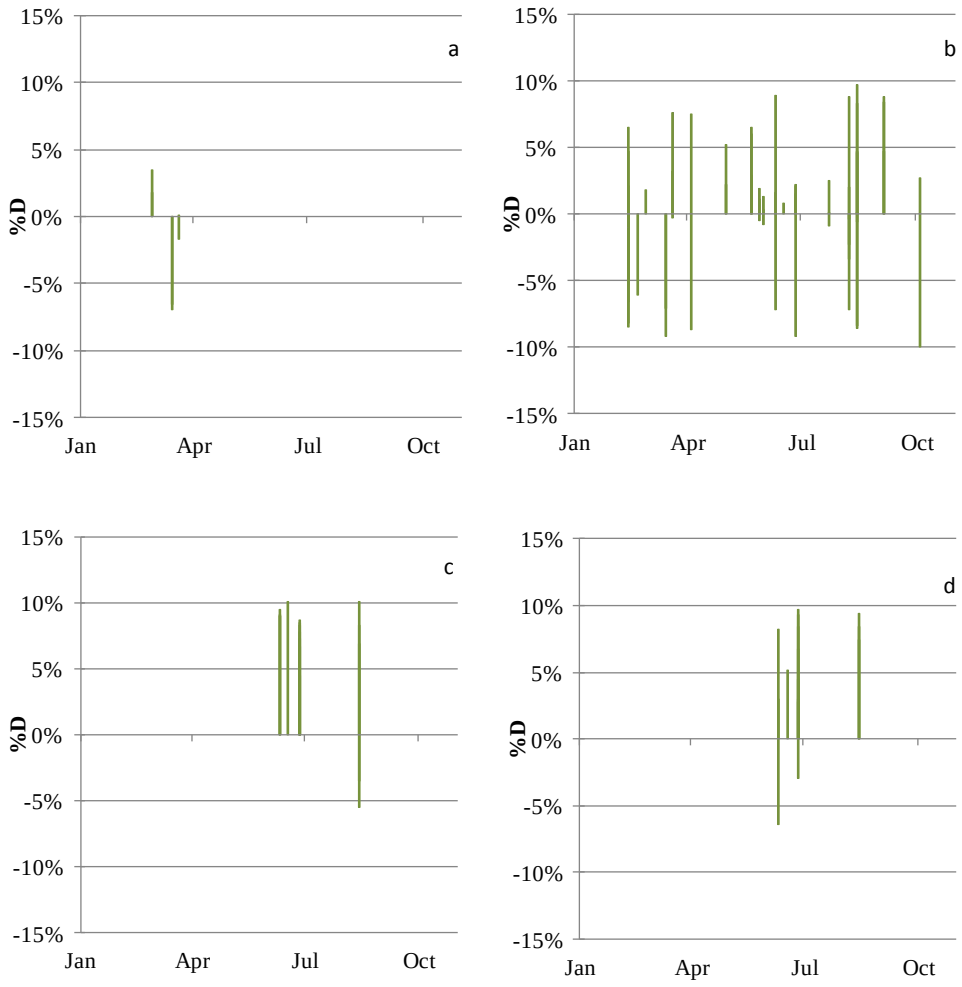

Figure C. Control charts for selected 2013 calibration control standards (CCS) for ICP-MS analyses: a) high concentration Se CCS (~0.04-0.2 mg/L), b) low concentration Se CCS (~0.002-0.02 mg/L), c) low concentration Cd CCS (~0.005 mg/L), and d) low concentration As CCS (~0.005 mg/L).

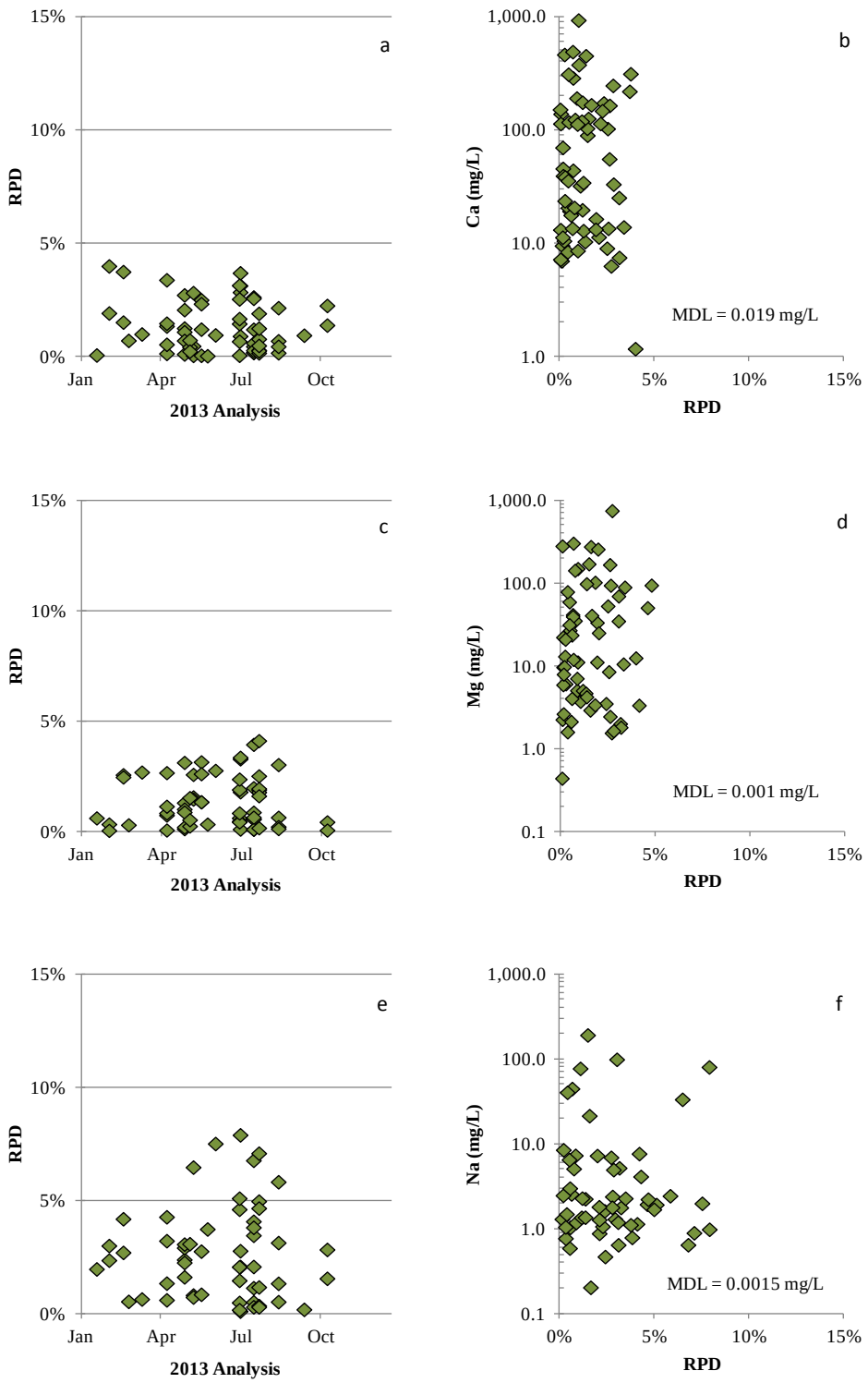

Figure D. Selected 2013 duplicates (Dups) for ICP-MS analyses: a) control chart for Ca, b) RPD for Dups versus concentration for Ca, c) control chart for Mg, d) RPD for Dups versus concentration for Mg, e) control chart for Na, and f) RPD for Dups versus concentration for Na.

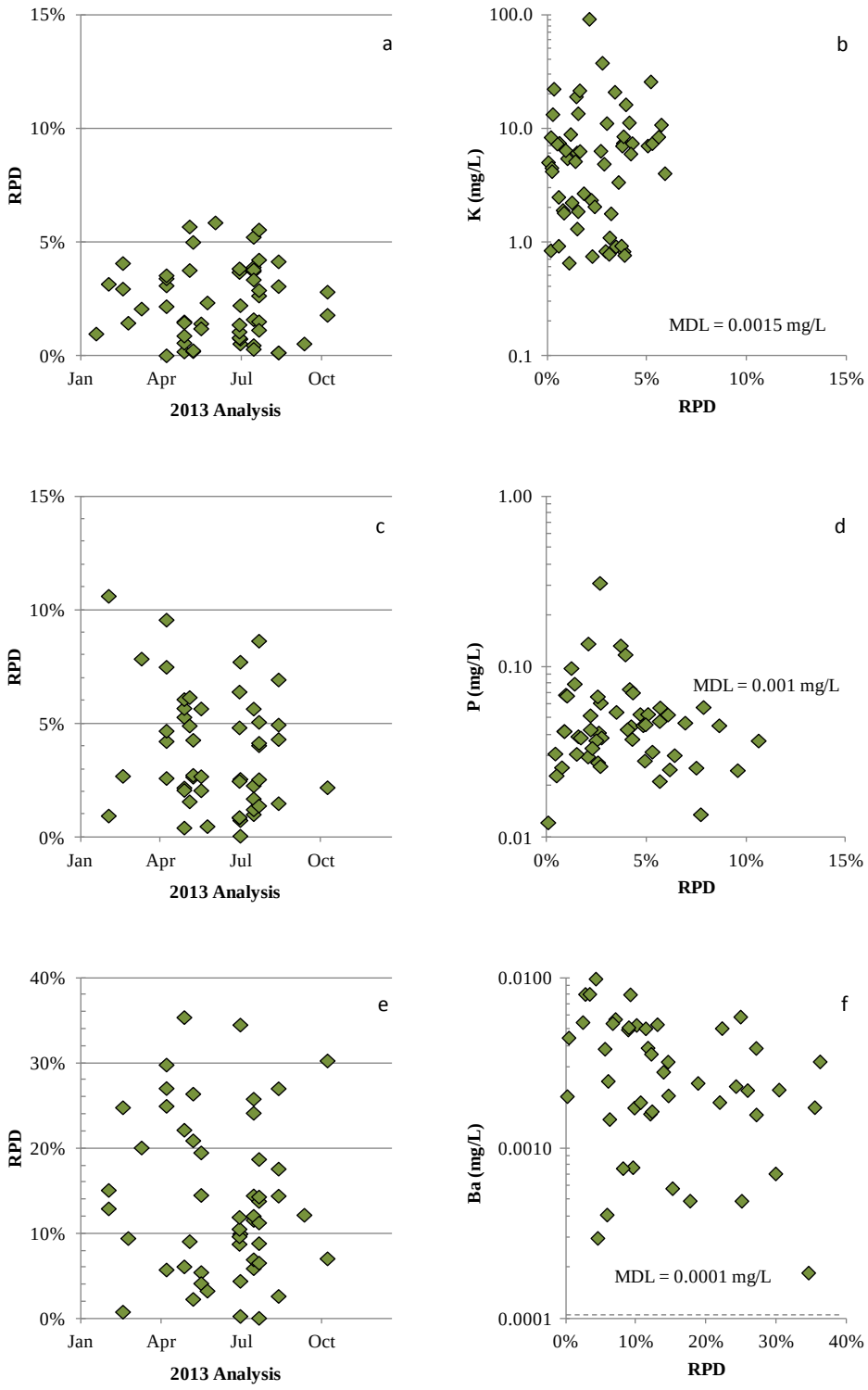

Figure E. Selected 2013 duplicates (Dups) for ICP-MS analyses: a) control chart for K, b) RPD for Dups versus concentration for K, c) control chart for P, d) RPD for Dups versus concentration for P, e) control chart for Ba, and f) RPD for Dups versus concentration for Ba.

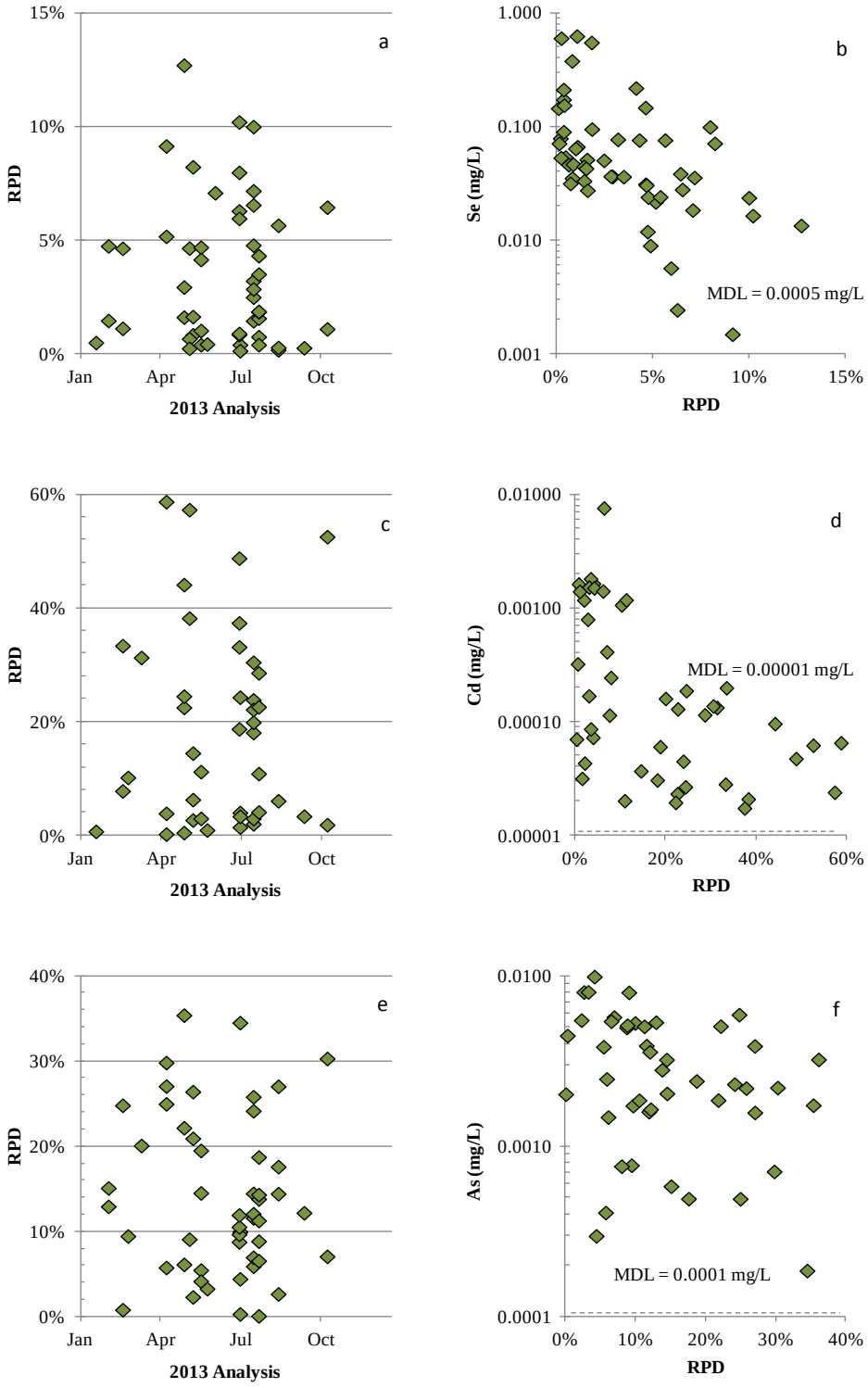

Figure F. Selected 2013 duplicates (Dups) for ICP-MS analyses: a) control chart for Se, b) RPD for Dups versus concentration for Se, c) control chart for Cd, d) RPD for Dups versus concentration for Cd, e) control chart for As, and f) RPD for Dups versus concentration for As.

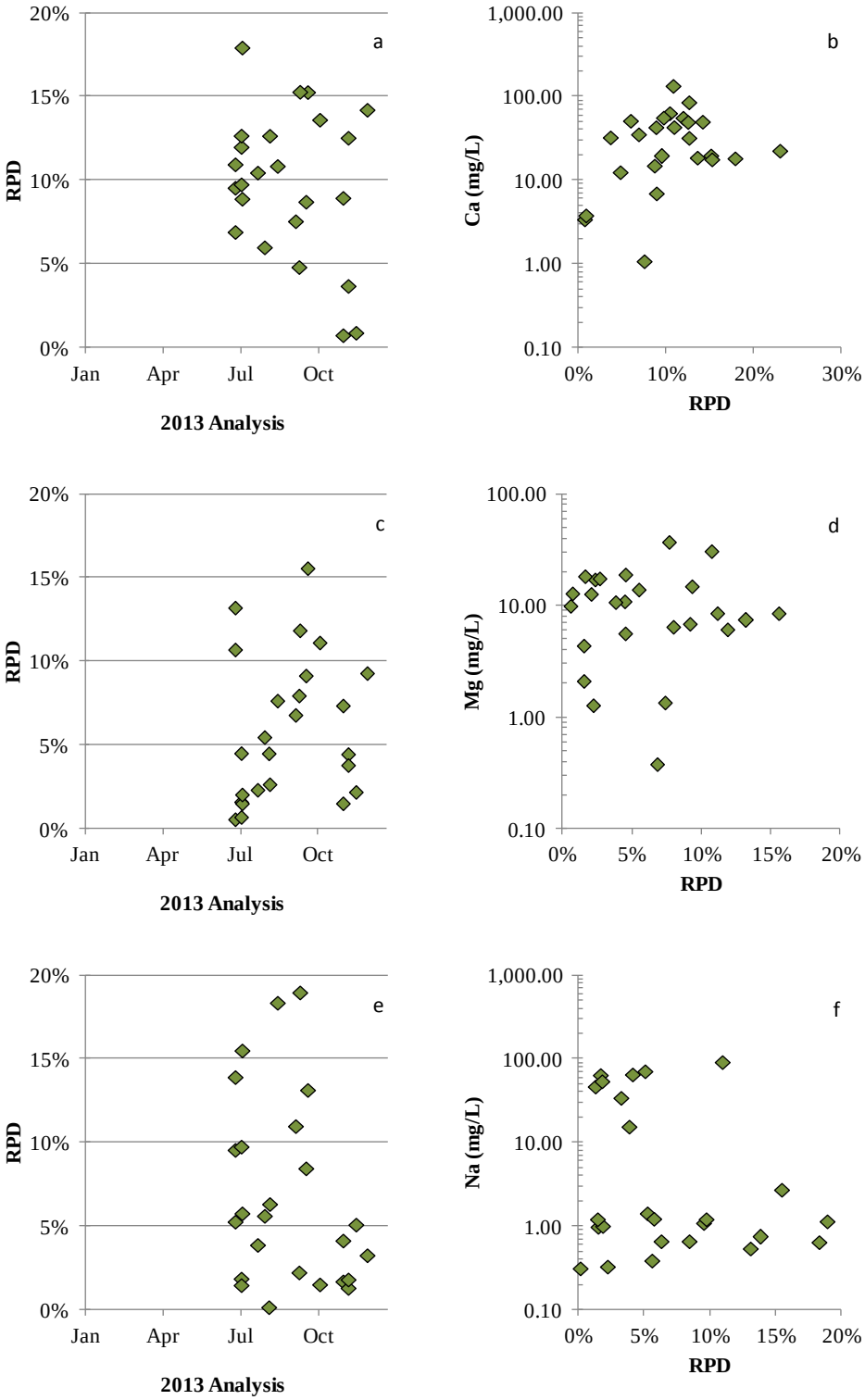

Figure G. Selected 2013 blind duplicates (BDups) for ICP-MS analyses: a) control chart for Ca, b) RPD for BDups versus concentration for Ca, c) control chart for Mg, d) RPD for BDups versus concentration for Mg, e) control chart for Na, and f) RPD for BDups versus concentration for Na.

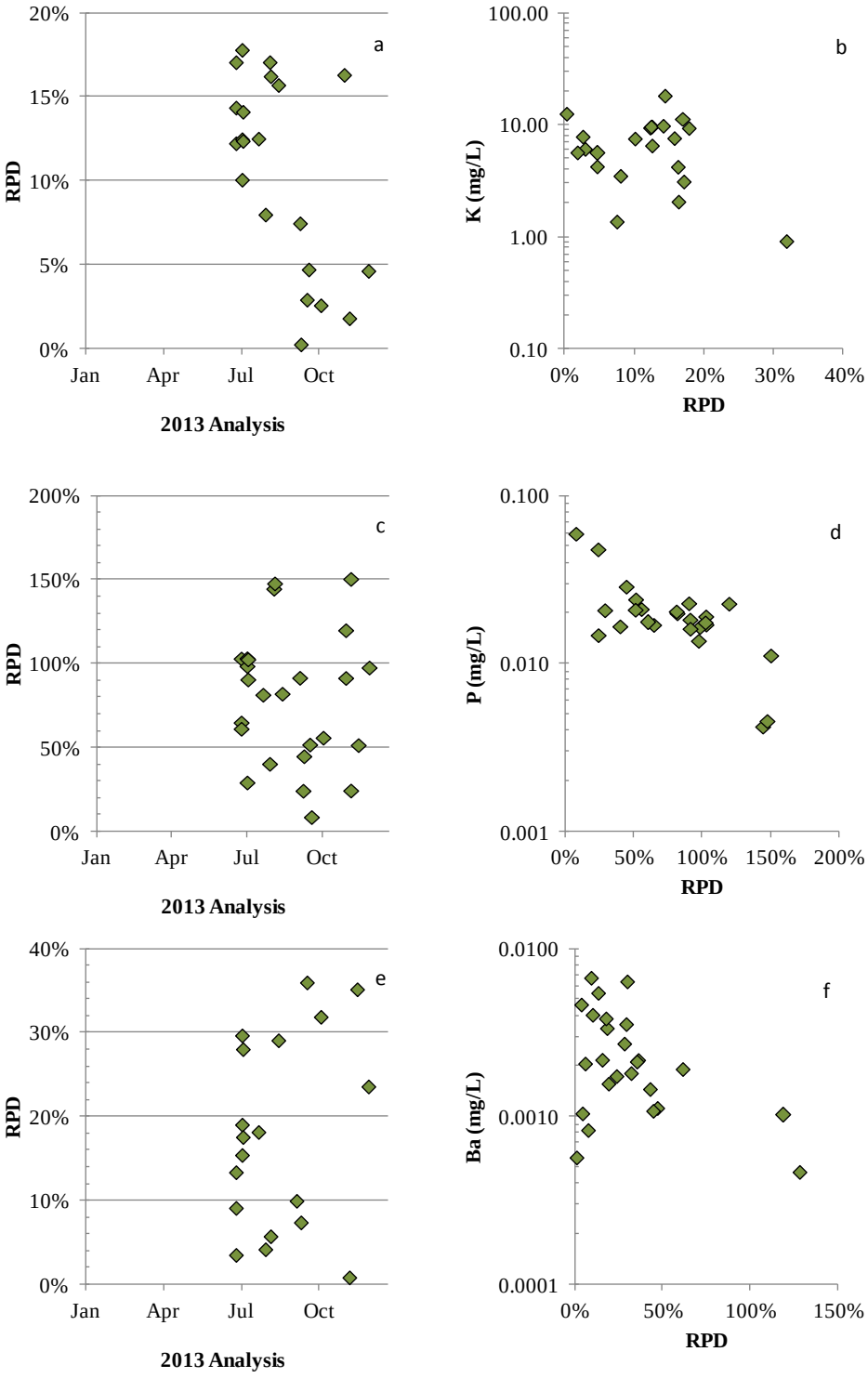

Figure H. Selected 2013 blind duplicates (BDups) for ICP-MS analyses: a) control chart for K, b) RPD for BDups versus concentration for K, c) control chart for P, d) RPD for BDups versus concentration for P, e) control chart for Ba, and f) RPD for BDups versus concentration for Ba.

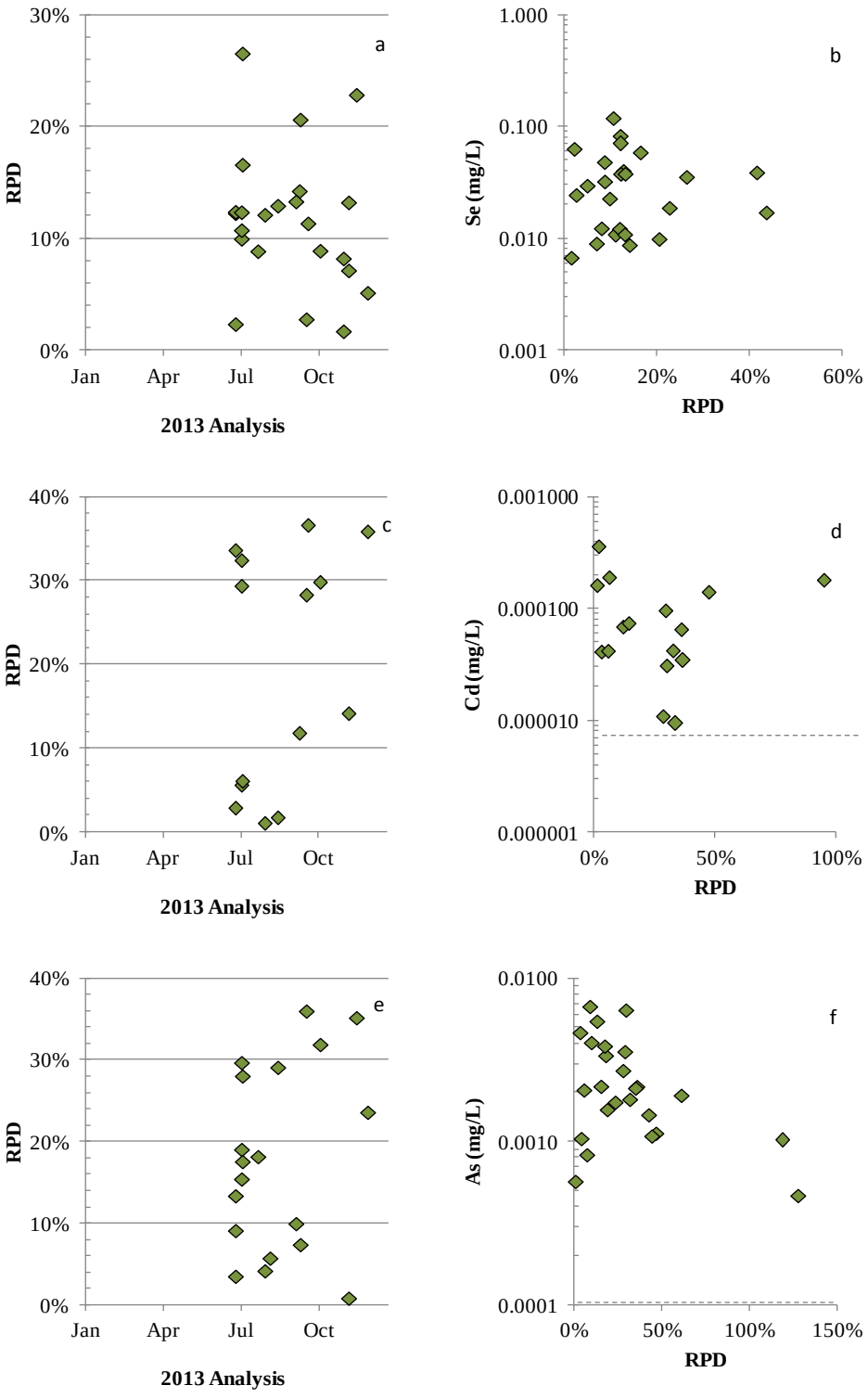

Figure I. Selected 2013 blind duplicates (BDups) for ICP-MS analyses: a) control chart for Se, b) RPD for BDups versus concentration for Se, c) control chart for Cd, d) RPD for BDups versus concentration for Cd, e) control chart for As, and f) RPD for BDups versus concentration for As.

Figure J. Control charts for selected 2013 calibration control standards (CCS) for ICP-OES analyses: a) high concentration Ca CCS (10 mg/L), b) low concentration Ca CCS (5 mg/L), c) high concentration Mg CCS (10 mg/L), d) low concentration Mg CCS (5 mg/L), e) high concentration Na CCS (1.0 mg/L), and f) low concentration Na (0.5 mg/L).

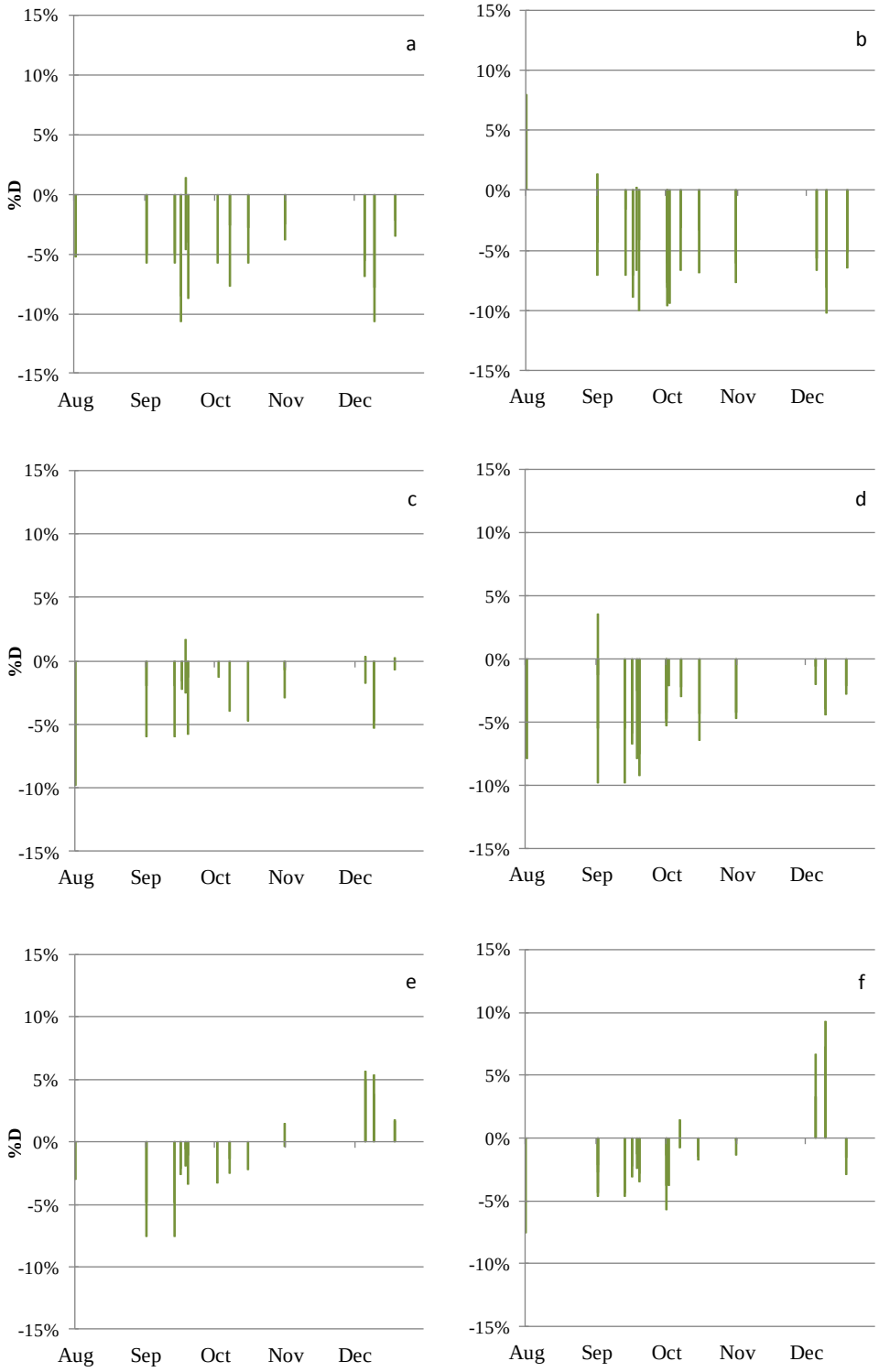

Figure K. Control charts for selected 2013 calibration control standards (CCS) for ICP-OES analyses: a) high concentration K CCS (1.0 mg/L), b) low concentration K CCS (0.5 mg/L), c) high concentration P CCS (0.1 mg/L), d) low concentration P CCS (0.05 mg/L), e) high concentration S CCS (10 mg/L), and f) low concentration S (5 mg/L).

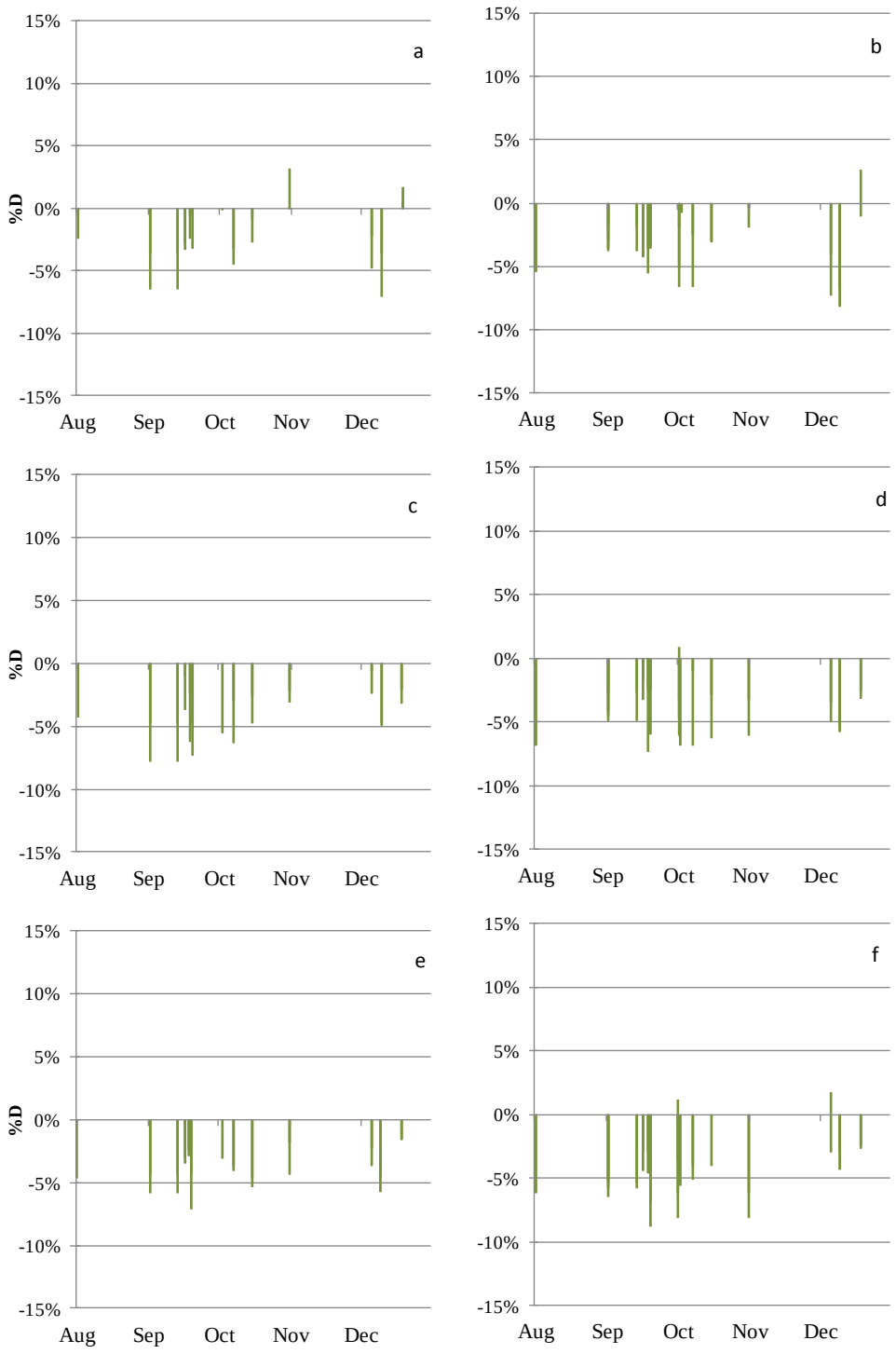

Figure L. Control charts for selected 2013 calibration control standards (CCS) for ICP-OES analyses: a) high concentration Se CCS (0.1 mg/L), b) low concentration Se CCS (0.05 mg/L), c) high concentration As CCS (0.1 mg/L), d) low concentration As CCS (0.05 mg/L), e) high concentration Cd CCS (0.1 mg/L), and f) low concentration Cd (0.05 mg/L).

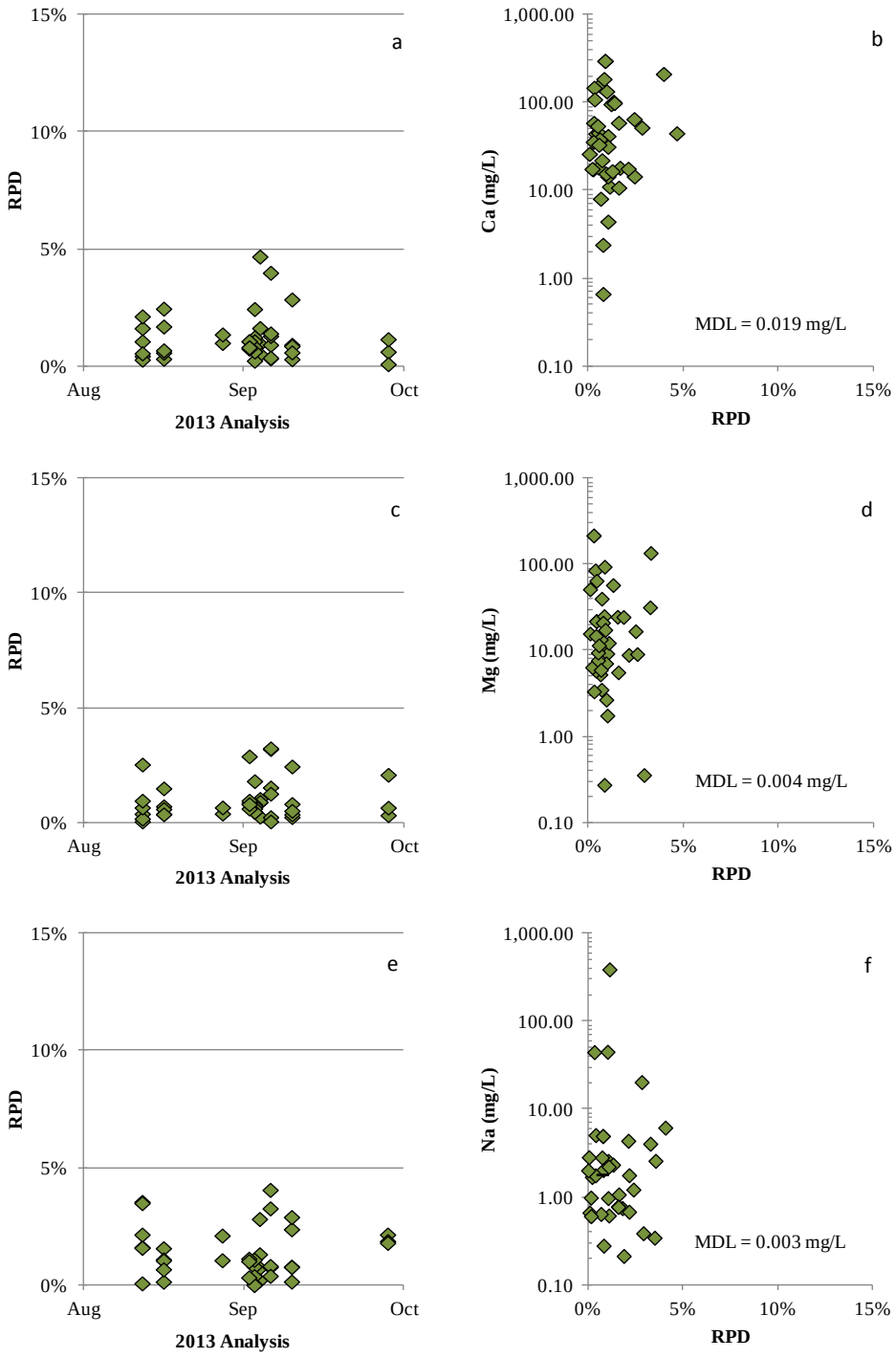

Figure M. Selected 2013 duplicates (Dups) for ICP-OES analyses: a) control chart for Ca, b) RPD for Dups versus concentration for Ca, c) control chart for Mg, d) RPD for Dups versus concentration for Mg, e) control chart for Na, and f) RPD for Dups versus concentration for Na.

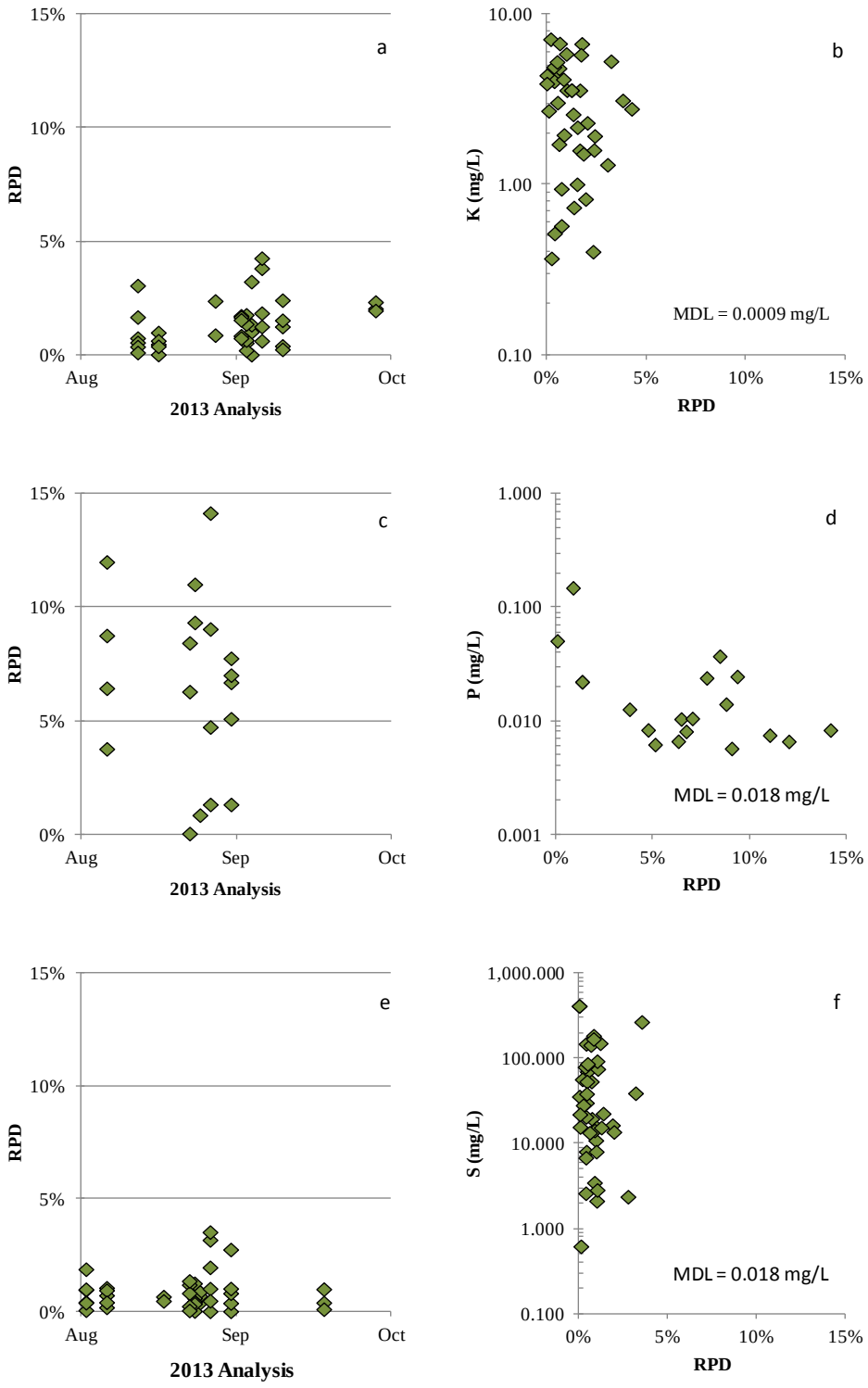

Figure N. Selected 2013 duplicates (Dups) for ICP-OES analyses: a) control chart for K, b) RPD for Dups versus concentration for K, c) control chart for P, d) RPD for Dups versus concentration for P, e) control chart for S, and f) RPD for Dups versus concentration for S.

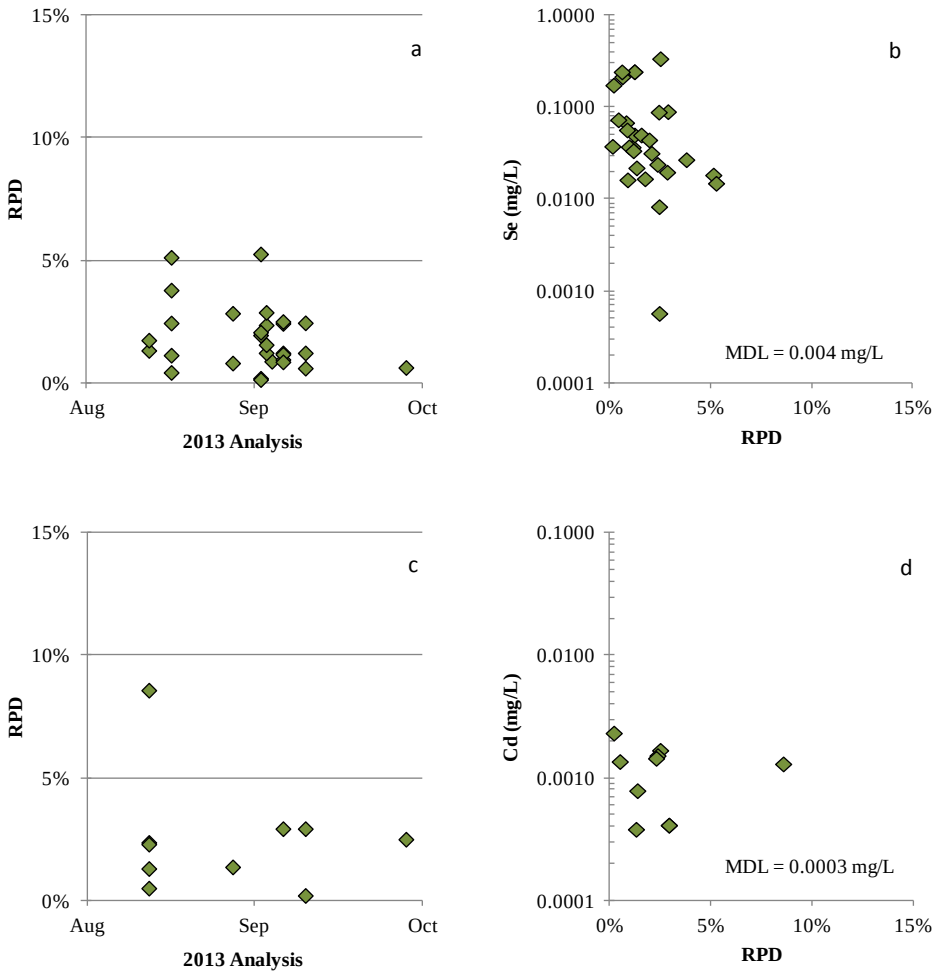

Figure O. Selected 2013 duplicates (Dups) for ICP-OES analyses: a) control chart for Se, b) RPD for Dups versus concentration for Se, c) control chart for Cd, and d) RPD for Dups versus concentration for Cd,

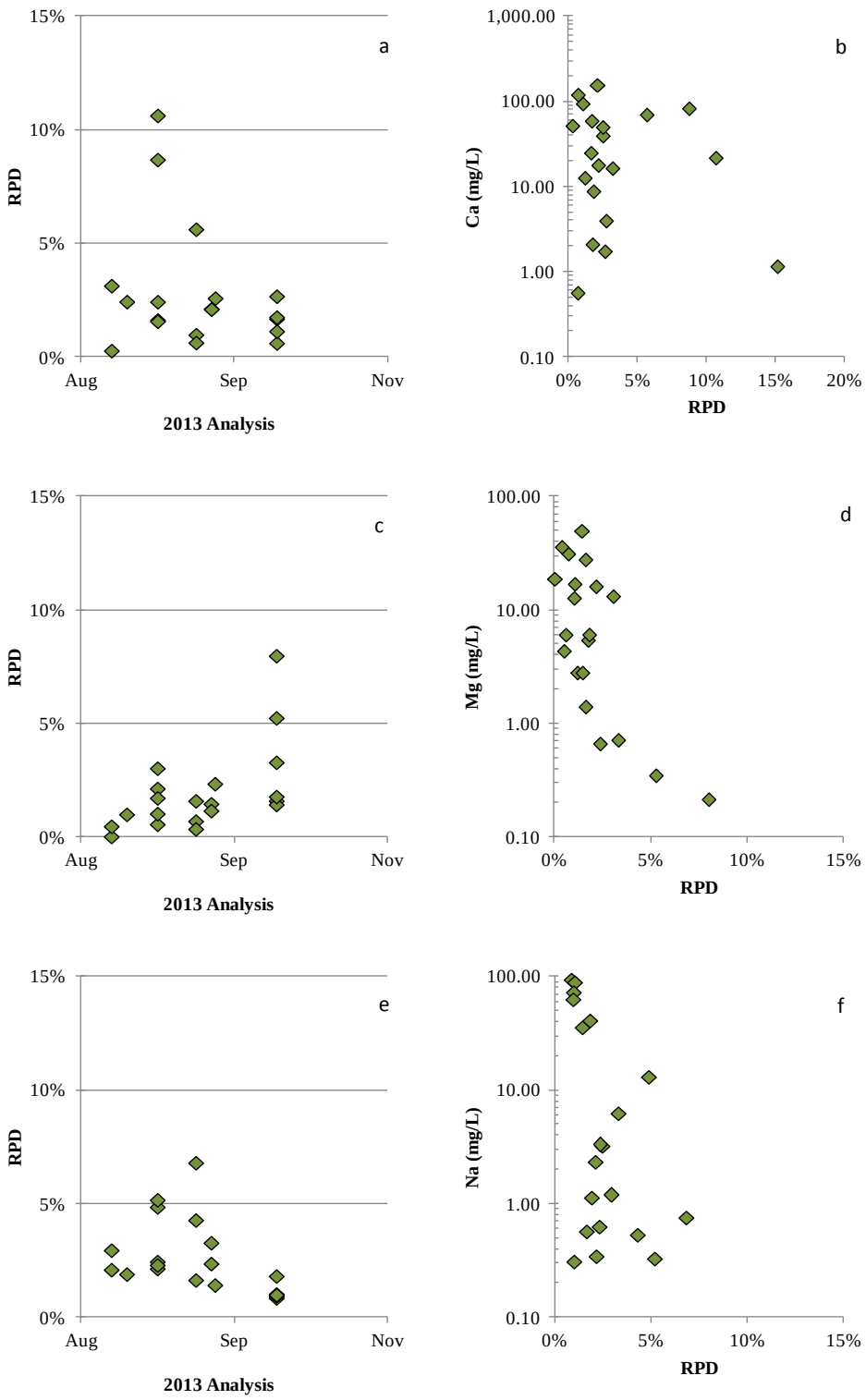

Figure P. Selected 2013 blind duplicates (BDups) for ICP-OES analyses: a) control chart for Ca, b) RPD for BDups versus concentration for Ca, c) control chart for Mg, d) RPD for BDups versus concentration for Mg, e) control chart for Na, and f) RPD for BDups versus concentration for Na.

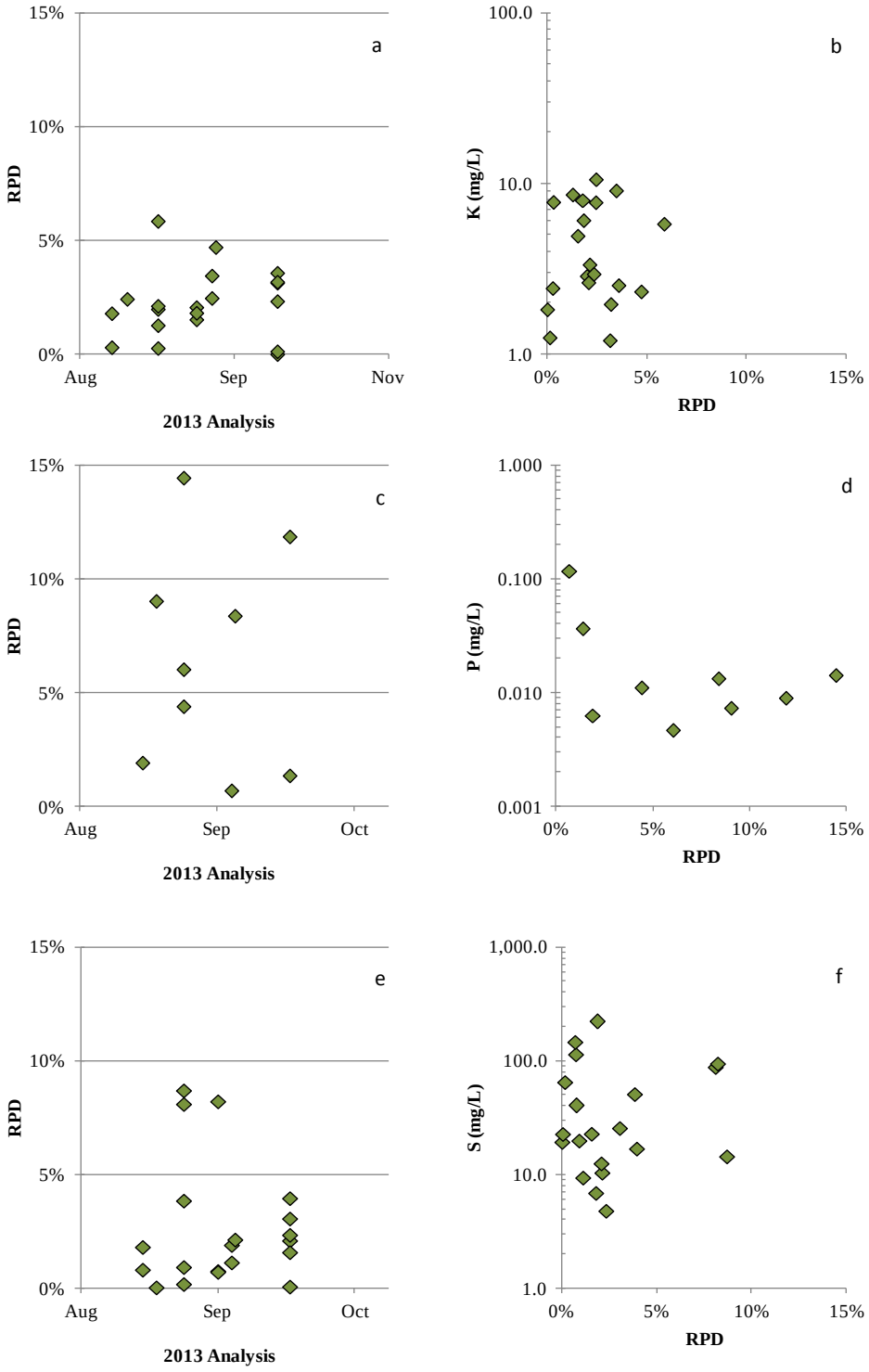

Figure Q. Selected 2013 blind duplicates (BDups) for ICP-OES analyses: a) control chart for K, b) RPD for BDups versus concentration for K, c) control chart for P, d) RPD for BDups versus concentration for P, e) control chart for S, and f) RPD for BDups versus concentration for S.

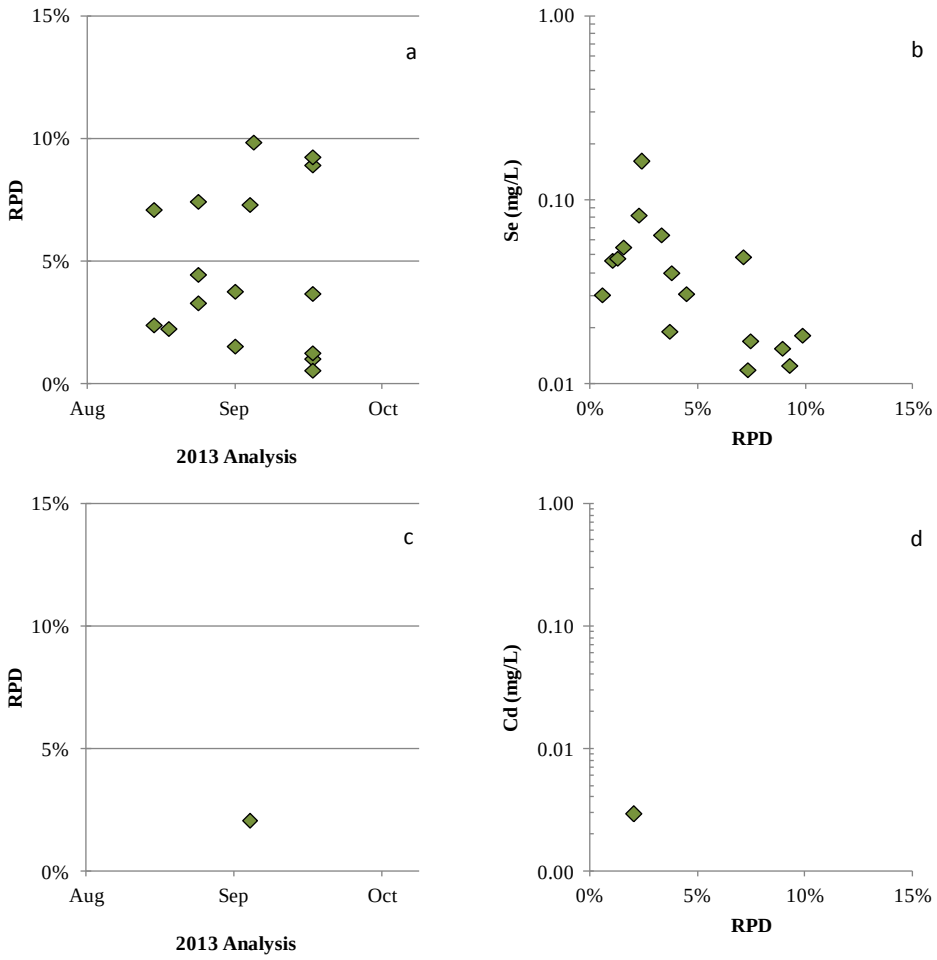

Figure R. Selected 2013 blind duplicates (BDups) for ICP-OES analyses: a) control chart for Se, b) RPD for BDups versus concentration for Se, c) control chart for Cd, and d) RPD for BDups versus concentration for Cd.

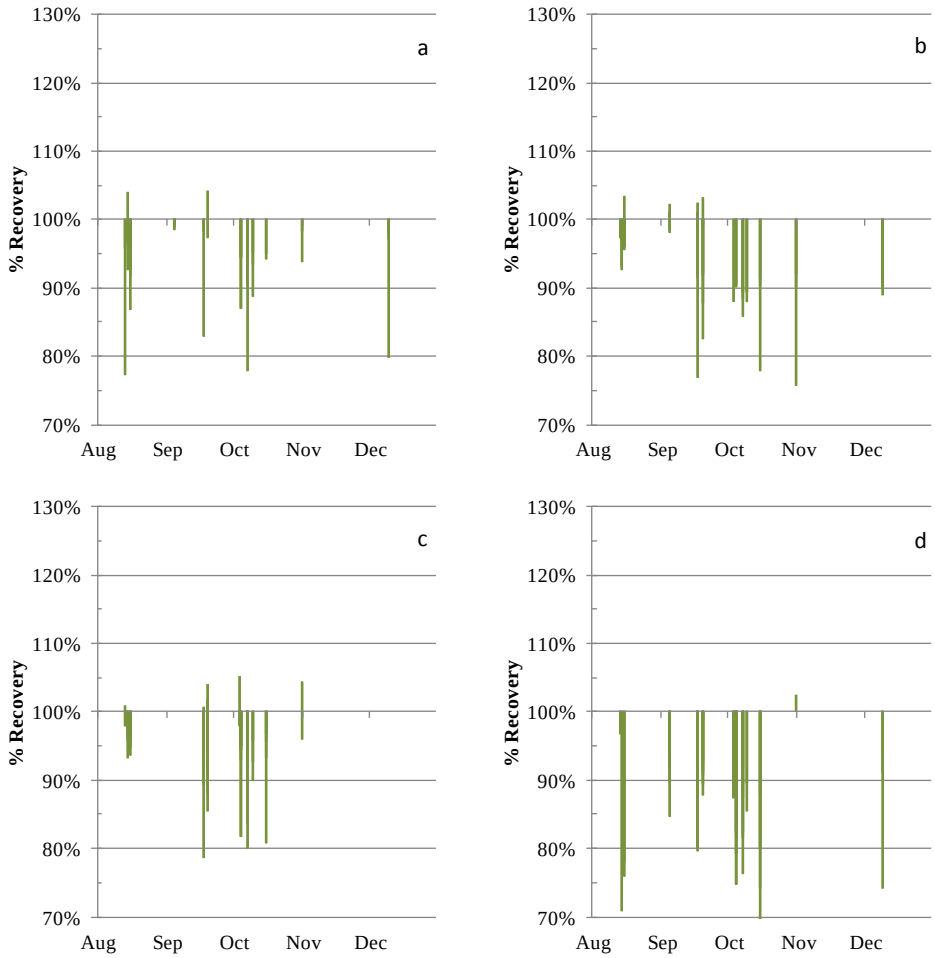

Figure S. Control charts for selected LFM %Recovery for ICP-OES analyses: a) Ca, b) Mg, c) Na, and d) K.

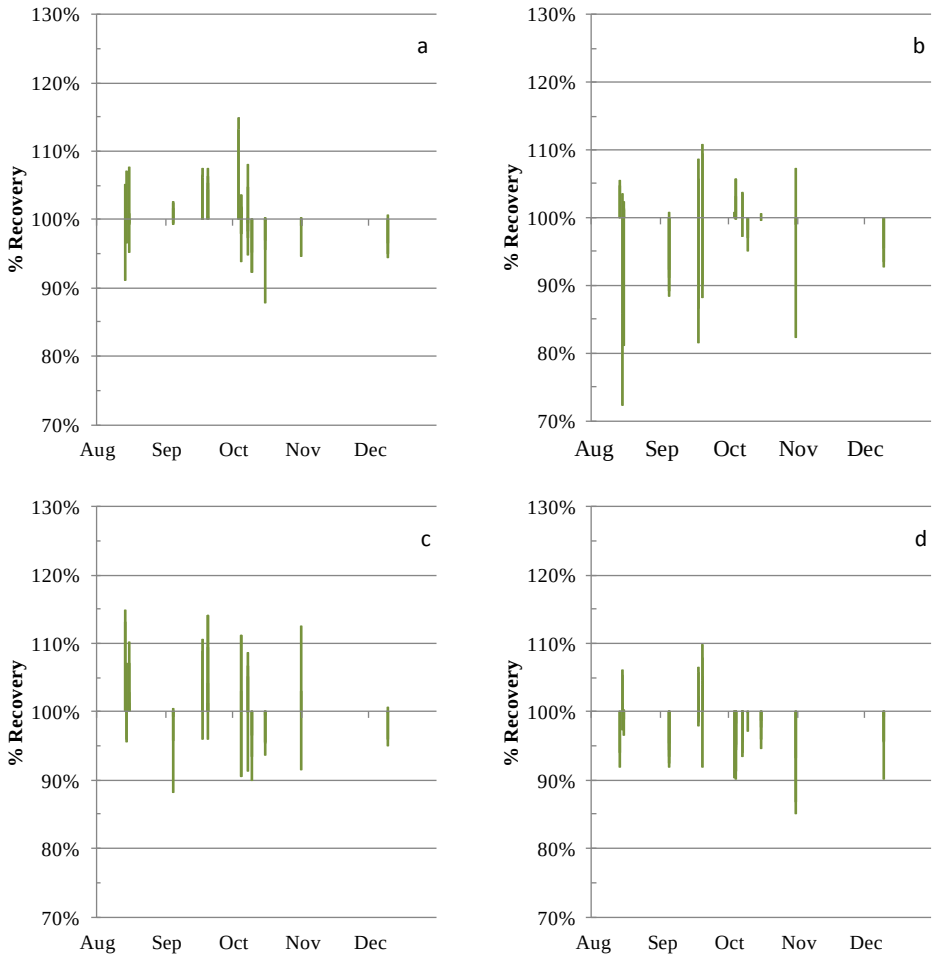

Figure T. Control charts for selected LFM %Recovery for ICP-OES analyses: a) P, b) S, c) Se, and d) Cd.

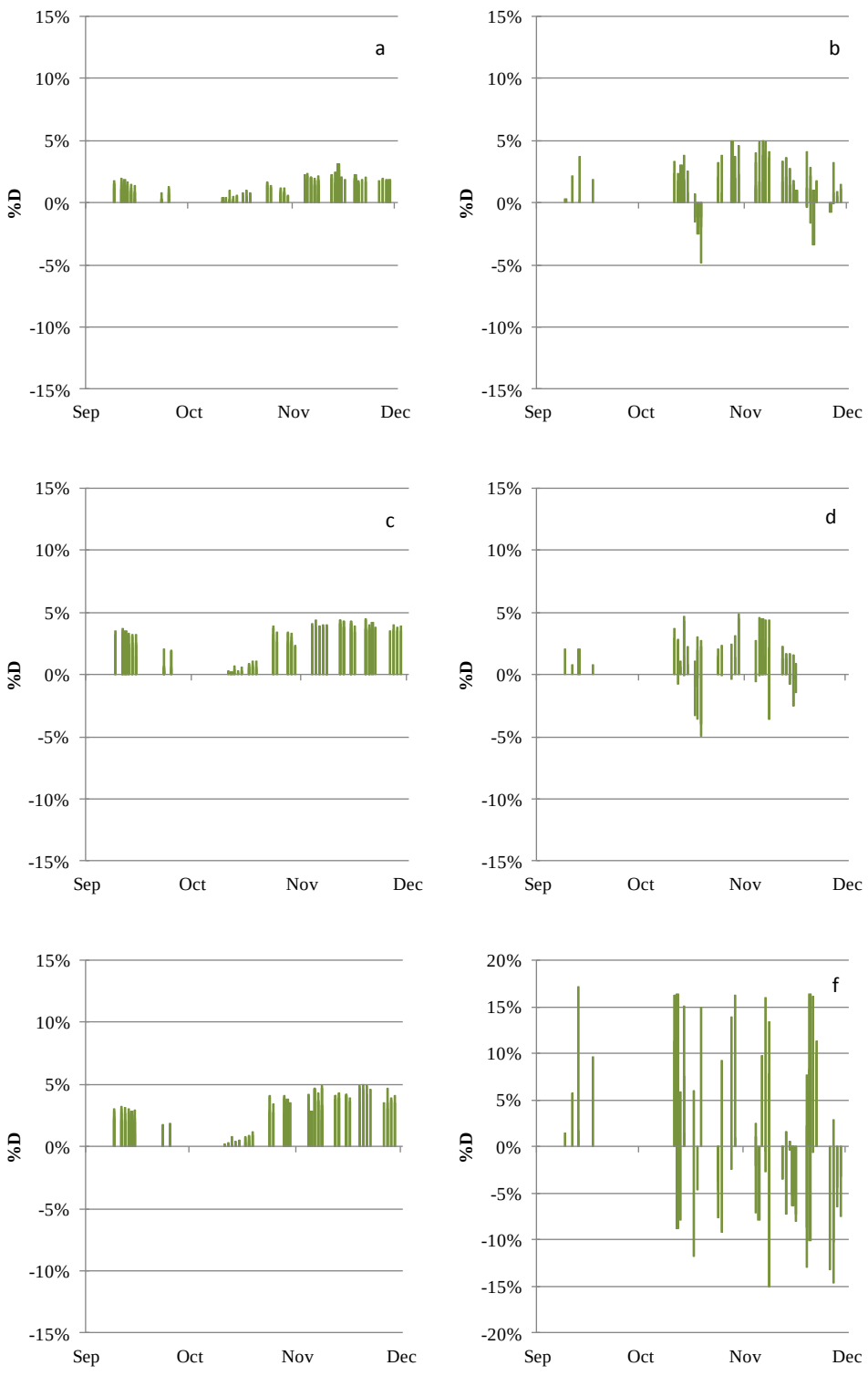

Figure U. Control charts for selected 2013 calibration control standards (CCS) for ICS analyses: a) high concentration Cl CCS (~115-300 mg/L), b) low concentration Cl CCS (~4.5 mg/L), c) high concentration NO_3 CCS (~30-75 mg/L), d) low concentration NO_3 CCS (~1.2 mg/L), e) high concentration SO_4 CCS (~115-300 mg/L), and f) low concentration SO_4 (~4.5 mg/L).

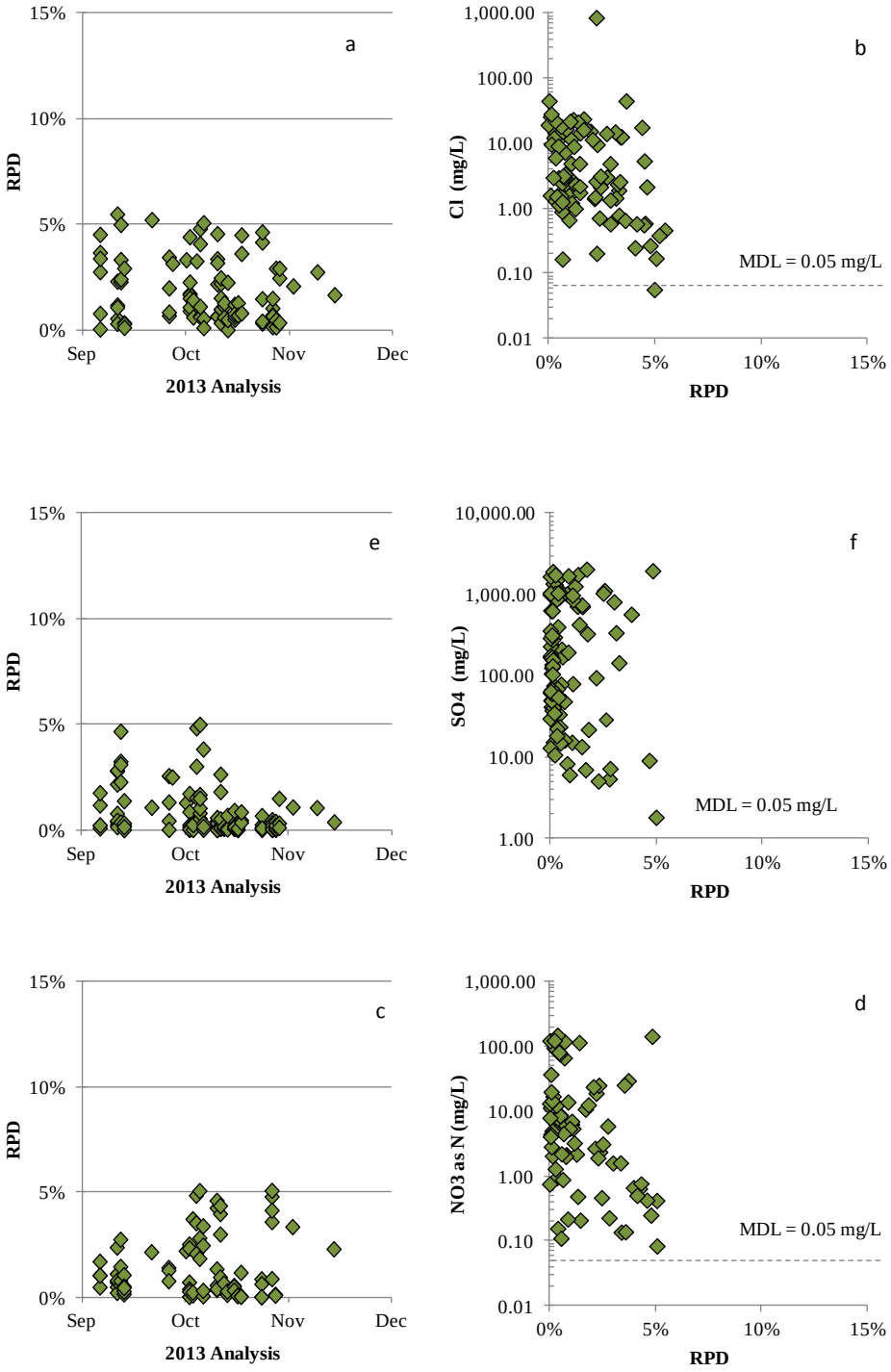

Figure V. Selected 2013 duplicates (Dups) for ICS analyses: a) control chart for Cl, b) RPD for Dups versus concentration for Cl, c) control chart for NO_3, d) RPD for Dups versus concentration for NO_3, e) control chart for SO_4, and f) RPD for Dups versus concentration for SO_4.

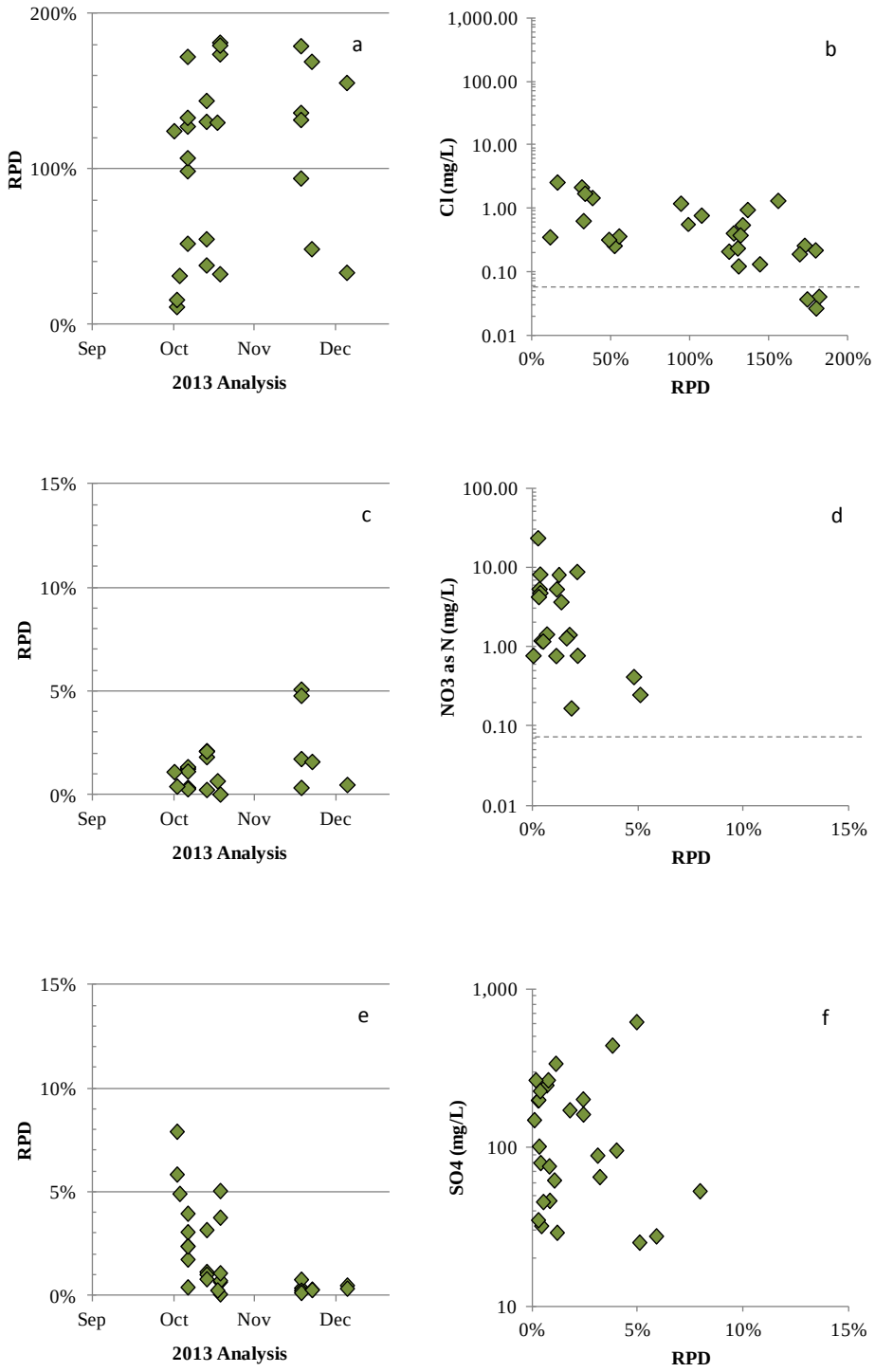

Figure W. Selected 2013 blind duplicates (BDups) for ICS analyses: a) control chart for Cl, b) RPD for BDups versus concentration for Cl, c) control chart for NO_3, d) RPD for BDups versus concentration for NO_3, e) control chart for SO_4, and f) RPD for BDups versus concentration for SO_4.

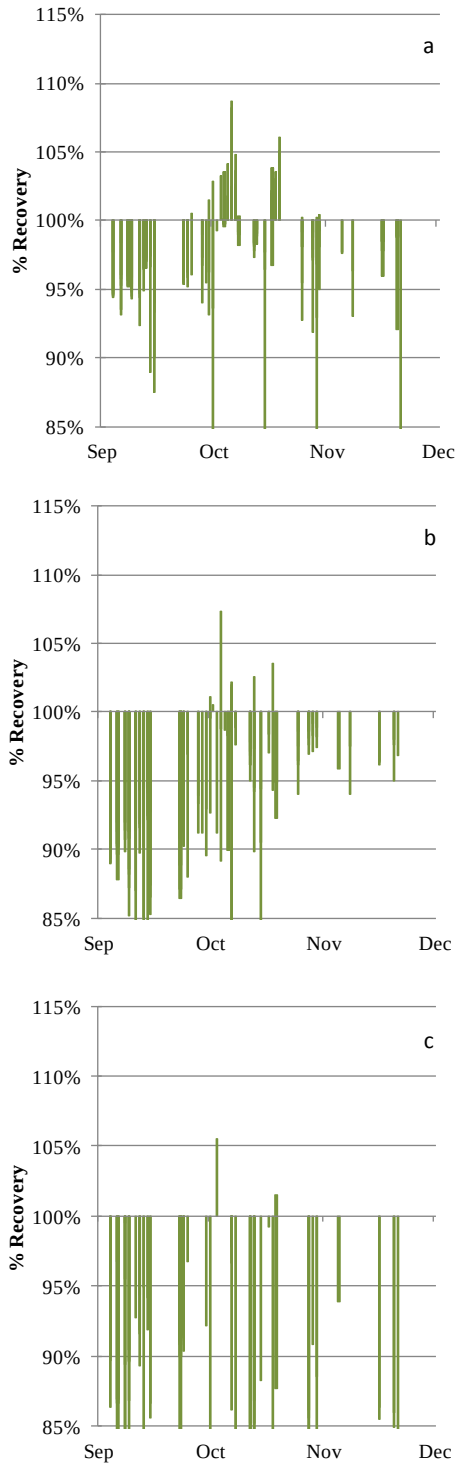

Figure X. Control charts for selected LFM %Recovery for ICS analyses: a) Cl, b) NO_3, and c) SO_4.

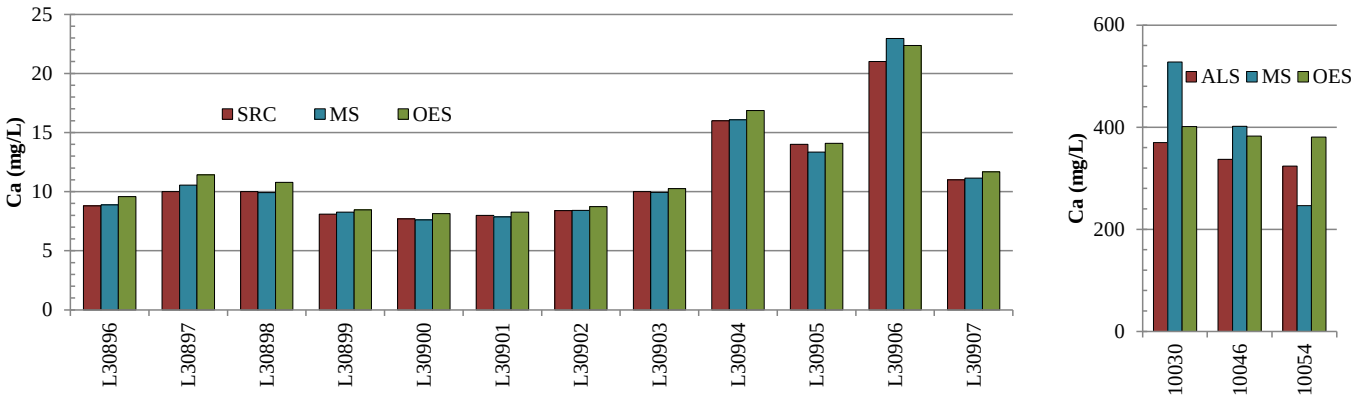

Figure Y. Inter-Lab comparison of Ca results.

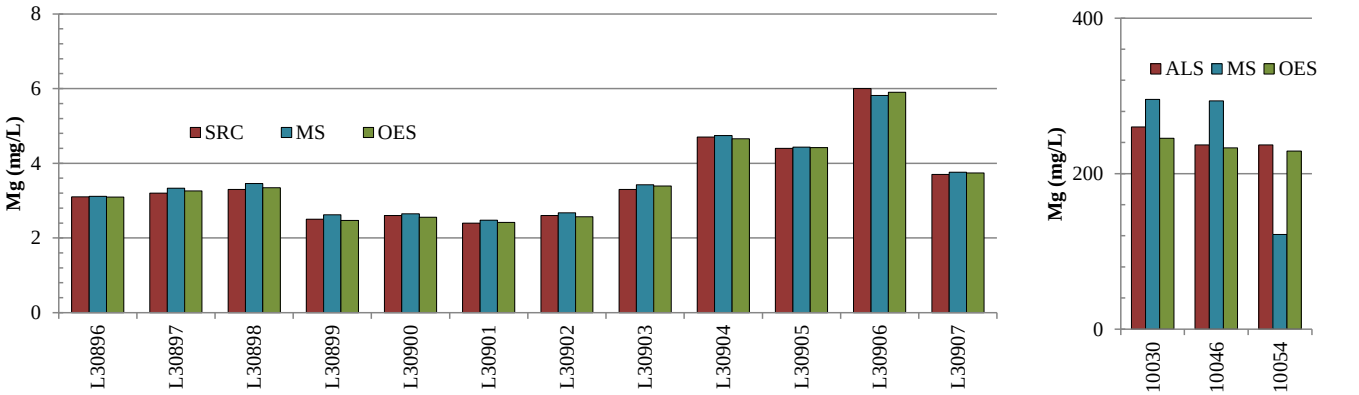

Figure Z. Inter-Lab comparison of Mg results.

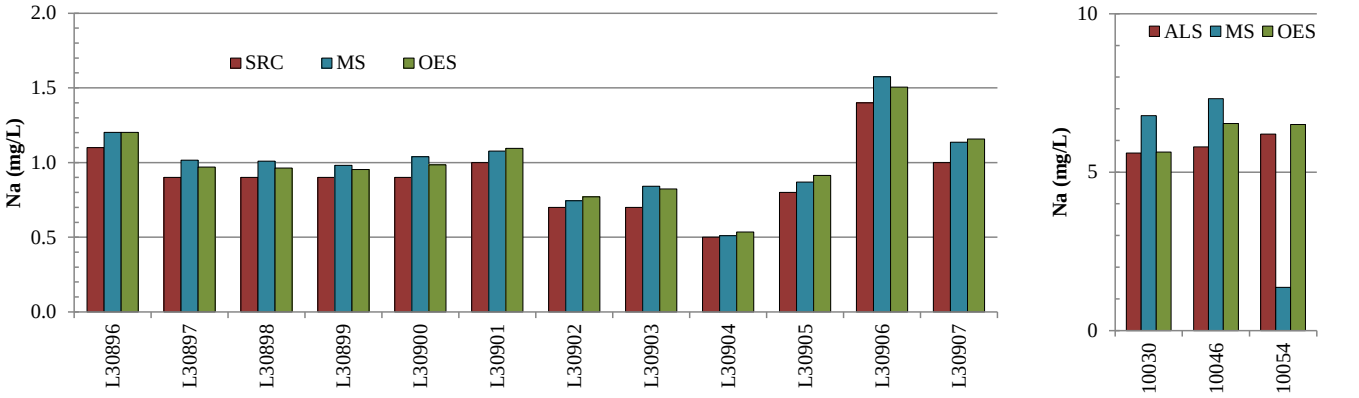

Figure AA. Inter-Lab comparison of Na results.

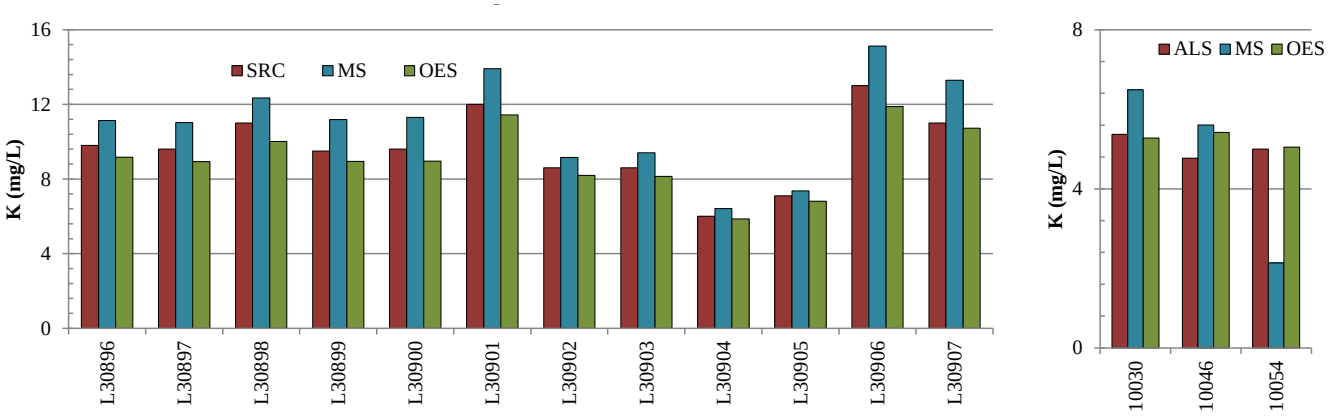

Figure AB. Inter-Lab comparison of K results.

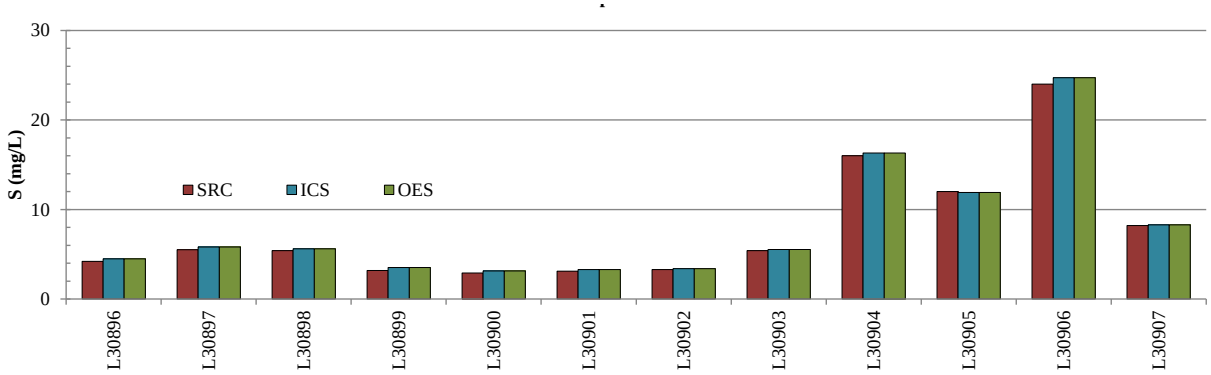

Figure AC. Inter-Lab comparison of S results.

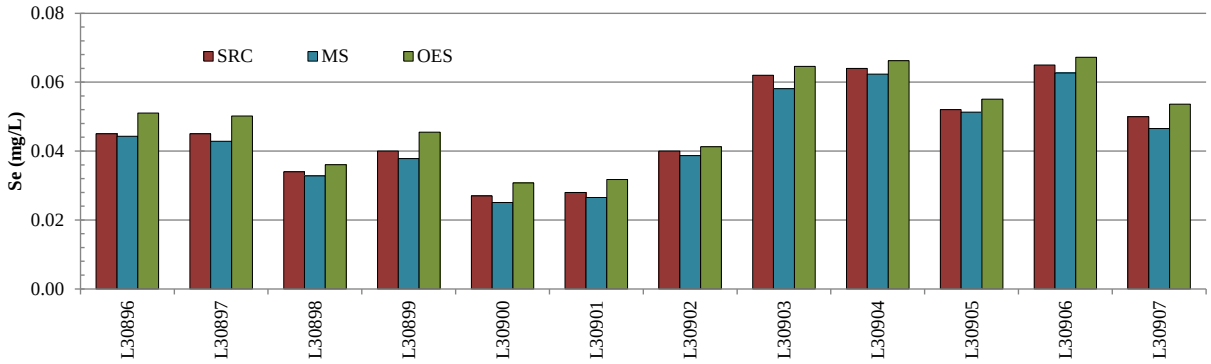

Figure AD. Inter-Lab comparison of Se results.

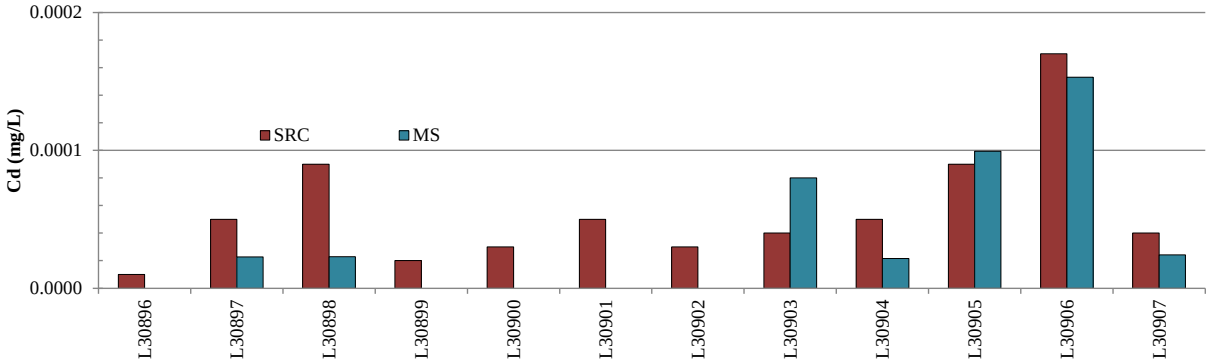

Figure AE. Inter-Lab comparison of As results.

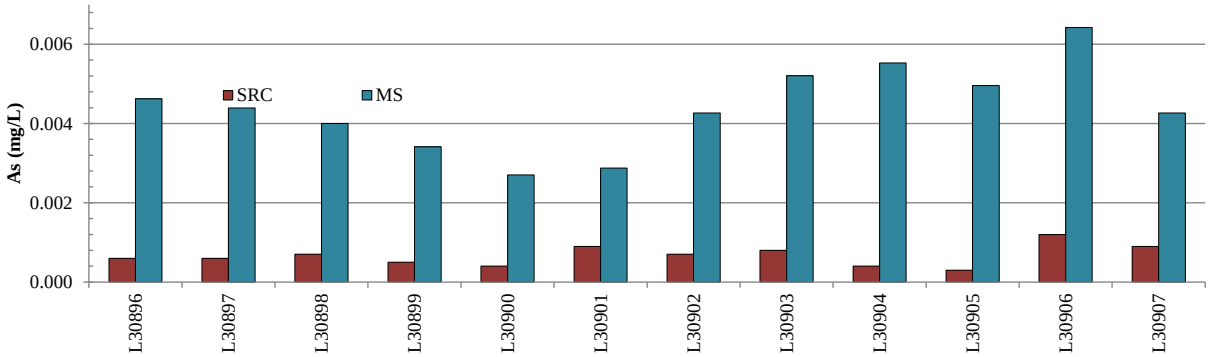

Figure AF. Inter-Lab comparison of Cd results.

APPENDIX B – DATA

ICS				
		MDL		
Duplicates		0.05	0.05	0.05
Date	**Sample ID**	**Chloride**	**Nitrate**	**Sulphate**
		mg/L Cl	mg/L N	mg/L SO4
08-Sep-13	30211A	44.69	6.32	216.12
08-Sep-13	30211A b	44.71	6.38	215.65
08-Sep-13	30240A (1)	7.27	0.12	1259.99
08-Sep-13	30240A (1) b	7.21	0.23	1245.28
08-Sep-13	30284A (2)	3.00	6.31	160.71
08-Sep-13	30284A (2) b	3.09	6.34	160.84
08-Sep-13	30699A	12.52	15.49	783.86
08-Sep-13	30699A b	12.10	14.54	732.15
08-Sep-13	30718A	5.33	10.78	328.24
08-Sep-13	30718A b	5.10	10.60	322.53
08-Sep-13	30211A	44.69	6.32	216.12
08-Sep-13	30211A b	44.71	6.38	215.65
13-Sep-13	10027	11.91	67.02	1172.95
13-Sep-13	10027 b	11.98	67.50	1177.39
13-Sep-13	10028	23.04	77.24	1319.37
13-Sep-13	10028 b	23.32	77.62	1322.50
13-Sep-13	12083	0.46	5.42	94.42
13-Sep-13	12083 b	0.48	5.36	92.39
13-Sep-13	12232	0.06		5.38
13-Sep-13	12232 b	0.07		5.24
13-Sep-13	12385	12.26	2.14	1011.15
13-Sep-13	12385 b	12.30	2.12	1003.33
13-Sep-13	12670	11.57	2.36	929.24
13-Sep-13	12670 b	11.45	2.41	925.15
13-Sep-13	12142	0.13	0.52	7.19
13-Sep-13	12142 b	0.09	0.56	6.99
13-Sep-13	10637	9.55	96.05	1693.74
13-Sep-13	10637 b	9.33	96.26	1696.15
14-Sep-13	12307	0.06	0.14	3.14
14-Sep-13	12307 b	0.06	0.13	2.97
14-Sep-13	12475	0.20	6.82	144.14
14-Sep-13	12475 b	0.21	6.78	139.54
14-Sep-13	12477	0.78	6.06	398.85
14-Sep-13	12477 b	0.75	6.01	397.40
14-Sep-13	12480		0.22	5.06

14-Sep-13	12480 b		0.24	5.18
14-Sep-13	12815	0.71	5.91	337.66
14-Sep-13	12815 b	0.72	5.75	327.34
14-Sep-13	12299	0.26	0.21	9.05
14-Sep-13	12299 b	0.23	0.21	8.64
15-Sep-13	10109	14.44	2.04	1001.09
15-Sep-13	10109 b	14.40	2.05	1001.07
15-Sep-13	12803			6.00
15-Sep-13	12803 b			5.71
15-Sep-13	19235	0.58	6.99	298.92
15-Sep-13	19235 b	0.56	6.91	299.53
15-Sep-13	19317	1.25	8.67	426.63
15-Sep-13	19317 b	1.08	8.63	420.80
15-Sep-13	10068	12.13	92.81	1513.09
15-Sep-13	10068 b	12.17	93.06	1517.90
15-Sep-13	10064	25.54	81.53	1359.24
15-Sep-13	10064 b	25.51	81.16	1357.27
23-Sep-13	10668	0.38	2.68	79.74
23-Sep-13	10668 R	0.40	2.74	78.89
28-Sep-13	10118	15.22	2.02	1060.70
28-Sep-13	10118 R	15.53	1.88	1065.29
28-Sep-13	10148	12.53	115.24	1757.00
28-Sep-13	10148 R	12.97	116.87	1780.21
28-Sep-13	10175	15.21	2.18	1047.96
28-Sep-13	10175 R	15.31	2.15	1048.10
28-Sep-13	10315	16.54	2.01	1114.29
28-Sep-13	10315 R	16.41	2.03	1086.11
28-Sep-13	19485	0.10		7.03
28-Sep-13	19485 R	0.12		6.54
29-Sep-13	10344	14.87	1.83	1034.80
29-Sep-13	10344 R	14.41	1.71	1009.25
03-Oct-13	10682	1.89	18.99	715.88
03-Oct-13	10682 R	1.83	18.58	706.76
04-Oct-13	10187	17.53	119.06	1692.32
04-Oct-13	10187 R	16.77	118.21	1677.93
04-Oct-13	10188	17.36	123.10	1664.50
04-Oct-13	10188 R	17.06	123.14	1664.70
04-Oct-13	10225	23.63	3.11	1031.29
04-Oct-13	10225 R	23.24	3.04	1033.72
04-Oct-13	10404	14.38	149.50	1907.59
04-Oct-13	10404 R	14.60	148.93	1905.14
04-Oct-13	10222	1.96	25.22	636.10
04-Oct-13	10222 R	1.94	25.81	635.87

04-Oct-13	30089A	4.87	4.89	466.51
04-Oct-13	30089A b	4.92	4.87	432.50
04-Oct-13	30170A	853.31	0.62	2041.08
04-Oct-13	30170A b	834.24	0.56	2006.35
05-Oct-13	10080	3.68	29.68	876.64
05-Oct-13	10080 R	3.20	28.60	879.37
05-Oct-13	10228	21.05	2.83	1033.88
05-Oct-13	10228 R	20.76	2.84	1034.00
05-Oct-13	10235	18.19	124.03	1741.91
05-Oct-13	10235 R	18.30	123.74	1737.62
06-Oct-13	10237	2.58	25.39	708.55
06-Oct-13	10237 R	2.43	24.51	719.39
06-Oct-13	10322	2.34	23.88	810.69
06-Oct-13	10322 R	2.27	23.39	835.47
06-Oct-13	10348	18.63	143.69	1954.18
06-Oct-13	10348 R	17.63	136.90	1862.02
07-Oct-13	19386	0.17		1.81
07-Oct-13	19386 R	0.17		1.72
07-Oct-13	19387	0.16		2.15
07-Oct-13	19387 R	0.21		1.94
07-Oct-13	19401	1.34	12.57	211.65
07-Oct-13	19401 R	1.33	12.34	212.80
07-Oct-13	19420	0.25		8.25
07-Oct-13	19420 R	0.24		8.32
07-Oct-13	19444	0.27	0.42	15.16
07-Oct-13	19444 R	0.28	0.44	15.32
07-Oct-13	19450	0.14	0.23	6.97
07-Oct-13	19450 R	0.16	0.23	7.09
07-Oct-13	19537	2.69	20.17	743.10
07-Oct-13	19537 R	2.72	21.44	732.10
08-Oct-13	19498	0.11	0.14	15.12
08-Oct-13	19498 R	0.07	0.13	15.08
08-Oct-13	19511	1.69	11.32	230.08
08-Oct-13	19511 R	1.68	11.32	230.03
08-Oct-13	19570	0.14	0.46	3.62
08-Oct-13	19570 R	0.13	0.45	3.33
08-Oct-13	19587	0.17	0.08	15.27
08-Oct-13	19587 R	0.18	0.11	15.29
08-Oct-13	19629 R	1.58	12.55	569.68
10-Oct-13	19629	1.58	12.51	548.30
12-Oct-13	L30343A	0.89	2.20	33.51
12-Oct-13	L30343A R	0.89	2.19	33.65
12-Oct-13	L32066A	0.58	0.64	136.54

12-Oct-13	L32066A R	0.61	0.61	136.42
12-Oct-13	L32076A	2.56	0.94	75.58
12-Oct-13	L32076A R	2.64	0.94	75.71
12-Oct-13	L32111A	1.16	0.42	48.18
19-Oct-13	L32111A R	1.23	0.44	48.33
12-Oct-13	L32121A	0.41	0.16	170.78
12-Oct-13	L32121A R	0.43	0.15	171.77
12-Oct-13	L32131A	1.44	0.62	169.39
12-Oct-13	L32131A R	1.48	0.55	169.41
12-Oct-13	L32142A	1.43	0.48	176.36
12-Oct-13	L32142A R	1.44	0.49	176.33
12-Oct-13	L32152A	1.41	0.14	62.03
12-Oct-13	L32152A R	1.44	0.15	62.04
13-Oct-13	L30359A	1.48	0.66	42.58
13-Oct-13	L30359A R	1.52	0.64	42.50
13-Oct-13	L30380A	1.57	1.59	41.36
13-Oct-13	L30380A R	1.58	1.54	41.33
13-Oct-13	L30418A	2.17	0.76	28.64
13-Oct-13	L30418A R	2.21	0.72	29.40
13-Oct-13	L30436A	2.13	5.40	21.77
13-Oct-13	L30436A R	2.18	5.35	21.38
13-Oct-13	L30445A	1.30	0.74	37.55
13-Oct-13	L30445A R	1.30	0.79	37.52
13-Oct-13	L30731A	0.66	0.15	78.49
13-Oct-13	L30731A R	0.65	0.13	78.89
14-Oct-13	L32215A	1.20		106.63
14-Oct-13	L32215A R	1.21		106.69
14-Oct-13	L32233A	0.99		167.96
14-Oct-13	L32233A R	0.97		167.84
14-Oct-13	L32242A (crushed)	1.55	4.52	40.48
14-Oct-13	L32242A (crushed) R	1.56	4.49	40.54
15-Oct-13	11078	19.14	17.03	277.77
15-Oct-13	11078 R	19.14	17.00	278.09
15-Oct-13	L30470A	2.93	4.99	50.00
15-Oct-13	L30470A R	2.92	5.00	49.98
15-Oct-13	L30472A	2.58	1.29	16.12
15-Oct-13	L30472A R	2.64	1.29	16.23
17-Oct-13	L30406A	0.17	0.11	34.11
17-Oct-13	L30406A R	0.20	0.11	34.17
17-Oct-13	L30522A	8.91	8.54	49.22
17-Oct-13	L30522A R	9.02	8.49	49.19
17-Oct-13	L30533A	1.13	12.32	65.00

17-Oct-13	L30533A R	1.12	12.36	65.03
17-Oct-13	L30709A	2.45	0.08	156.17
17-Oct-13	L30709A R	2.44	0.07	155.97
17-Oct-13	L32224A (1)	2.96		6.06
17-Oct-13	L32224A (1) R	2.98		6.01
18-Oct-13	L30462A	2.32	4.41	29.70
18-Oct-13	L30462A R	2.35	4.40	29.70
18-Oct-13	L30509A	3.07	37.24	125.37
18-Oct-13	L30509A R	3.05	37.21	125.27
19-Oct-13	L30554A	0.65	3.24	23.42
19-Oct-13	L30554A R	0.67	3.27	23.53
19-Oct-13	L30579A	3.35	4.07	69.39
19-Oct-13	L30579A R	3.32	4.07	69.63
19-Oct-13	L30591A	0.56	7.94	194.62
19-Oct-13	L30591A R	0.58	7.94	196.27
25-Oct-13	C32265A	22.00	0.22	358.66
25-Oct-13	C32265A R	22.07	0.22	358.62
25-Oct-13	L30622A		0.88	67.42
25-Oct-13	L30622A R		0.87	67.36
25-Oct-13	L30633A	0.58	0.75	61.38
25-Oct-13	L30633A R	0.60	0.75	61.23
25-Oct-13	L30644A	2.13	13.19	131.73
25-Oct-13	L30644A R	2.23	13.19	131.88
25-Oct-13	L32283A	4.86	0.17	48.25
25-Oct-13	L32283A R	4.93	0.15	47.93
25-Oct-13	L32294A	1.52	0.16	60.25
25-Oct-13	L32294A R	1.53	0.15	60.20
28-Oct-13	C32161A	21.71	13.89	630.16
28-Oct-13	C32161A R	21.93	14.02	629.52
28-Oct-13	L32010A	3.15	0.14	14.89
28-Oct-13	L32010A R	3.17	0.13	14.96
28-Oct-13	L32028A	2.97	0.25	22.31
28-Oct-13	L32028A R	2.96	0.26	22.24
28-Oct-13	L32162A	1.74	0.50	34.64
28-Oct-13	L32162A R	1.71	0.48	34.71
28-Oct-13	L32172A	1.25		12.97
28-Oct-13	L32172A R	1.26		12.97
28-Oct-13	L32267A	9.61	0.08	64.00
28-Oct-13	L32267A R	9.60	0.09	63.98
29-Oct-13	11158	28.07	14.51	290.60
29-Oct-13	11158 R	28.11	14.50	290.63
29-Oct-13	11194	9.05	19.99	314.91
29-Oct-13	11194 R	9.01	19.97	314.65

29-Oct-13	L32034A	4.84		54.40
29-Oct-13	L32034A R	4.99		54.61
29-Oct-13	L32045A	0.59		10.63
29-Oct-13	L32045A R	0.63		10.65
30-Oct-13	L30757A	3.11	0.16	18.31
30-Oct-13	L30757A R	3.19	0.17	18.36
30-Oct-13	L30769A	5.97	0.11	104.28
30-Oct-13	L30769A R	5.99	0.10	104.39
30-Oct-13	L32017A	1.34	0.12	13.41
30-Oct-13	L32017A R	1.38	0.10	13.21
03-Nov-13	10388	11.38	1.60	856.48
03-Nov-13	10388 R	11.62	1.54	865.77
10-Nov-13	10435	14.09	1.87	978.71
10-Nov-13	10435 R	14.48	1.67	968.50
15-Nov-13	10436	16.14	1.91	1039.72
15-Nov-13	10436 R	15.87	1.87	1043.59

Blind Duplicates				
Date	**Sample ID**	**Chloride**	**Nitrate**	**Sulphate**
18-Oct-13	July 15/13 BD	0.55	7.97	161.63
18-Oct-13	L30508A	1.63	7.87	157.80
18-Oct-13	July 16/13 BD	0.25	5.32	31.98
17-Oct-13	L30528A	3.44	5.34	32.11
18-Oct-13	July 17/13 BD	0.76	4.74	95.70
17-Oct-13	L30544A	2.52	4.73	91.98
18-Oct-13	July 21/13 BD	0.25	4.24	171.88
19-Oct-13	L30571A	0.43	4.25	174.92
18-Oct-13	July 22/13 BD	0.40	3.65	88.90
19-Oct-13	L30581A	1.81	3.70	91.67
18-Oct-13	Aug.13/13 BD	0.54	5.29	201.11
17-Oct-13	L30691A	2.69	5.23	196.37
14-Oct-13	Aug. 14/13 BD	0.35	1.19	52.99
13-Oct-13	L30734A	0.39	1.19	57.36
30-Oct-13	Aug. 21/13 BD	0.04	0.77	148.90
30-Oct-13	L30754A	0.83	0.77	149.01
30-Oct-13	Aug. 27/13 BD		0.30	246.86
30-Oct-13	L30766A		0.32	245.22
30-Oct-13	Aug. 28/13 BD			265.74
07-Nov-13	L30773A	0.45	0.45	263.80
30-Oct-13	Sept. 3/13 BD	0.04	0.06	337.68
07-Nov-13	L30774A	0.52	0.60	334.01
30-Oct-13	Sept. 5/13 BD	0.03	0.09	439.66
08-Nov-13	L30779A	0.49	0.10	423.36
15-Oct-13	Sept. 9/13 BD	2.12		618.60
08-Nov-13	L30788A	1.54	0.10	649.82
14-Oct-13	Sept. 10/13 BD	2.54	0.68	27.54
14-Oct-13	L30742A	2.16	0.14	25.97
30-Oct-13	Sept. 11/13 BD	0.62	4.65	25.13

13-Oct-13	L30736A	0.87	5.76	26.44
25-Oct-13	Sept. 13/13 BD	0.13	0.17	29.00
25-Oct-13	L30625A	0.80	0.16	28.66
13-Oct-13	Sept. 16/13 BD	0.21	0.24	40.10
25-Oct-13	L30627A	0.89	0.20	33.59
25-Oct-13	Sept. 17/13 BD	0.12	0.77	62.01
25-Oct-13	L30633A	0.58	0.75	61.38
25-Oct-13	Sept. 23/13 BD	0.36	8.77	65.10
25-Oct-13	L30635A	0.63	8.59	63.07
25-Oct-13	Sept. 26/13 BD	1.44	23.39	46.11
25-Oct-13	L30643A	2.13	23.33	45.74
13-Oct-13	Sept. 30/13 BD		0.76	11.70
12-Oct-13	L30348A		0.75	9.65
29-Oct-13	Oct. 24/13 BD	0.23	1.43	34.80
29-Oct-13	L30451A	1.09	1.44	34.71
29-Nov-13	Nov 18/13 BD	0.93	8.14	79.86
29-Nov-13	L30647A	4.94	8.17	79.56
29-Nov-13	Nov 20/13 BD	0.37	1.41	76.09
29-Nov-13	L30652A	1.81	1.43	75.50
29-Nov-13	Nov 21/13 BD	0.22	0.25	198.25
29-Nov-13	L30655A	3.96	0.23	197.76
29-Nov-13	Nov 25/13 BD	1.18	0.41	265.57
29-Nov-13	L30661A	3.27	0.40	265.19
03-Dec-13	Nov 27/13 BD	0.32	1.28	101.46
03-Dec-13	L30667A	0.52	1.30	101.15
03-Dec-13	Nov 28/13 BD	0.19	0.10	199.29
03-Dec-13	L30673A	2.26	0.12	198.72
16-Dec-13	BD Dec 2/13	1.30		45.34
16-Dec-13	L30674A	10.44		45.56
16-Dec-13	BD Dec 10/13	1.69	1.16	226.87
16-Dec-13	L30680A	2.37	1.16	226.07

Calibration Control Standards	Calculated CCS	Chloride	Nitrate	Sulphate
	CCS 1	290.7957	72.6989	290.7957

Date	Measured CCS	Chloride	Nitrate	Sulphate
09-Sep-13	CCS 1	285.62	70.11	282.03
09-Sep-13	CCS 1	285.67	70.15	281.90
09-Sep-13	CCS 1	286.52	70.37	282.53
09-Sep-13	CCS 1	286.31	70.42	283.66
09-Sep-13	CCS 1	287.33	70.65	284.13
09-Sep-13	CCS 1	287.39	70.60	284.60
11-Sep-13	CCS 1	285.93	70.11	281.86
11-Sep-13	CCS 1	286.72	70.44	282.70
11-Sep-13	CCS 1	285.18	70.00	281.47
11-Sep-13	CCS 1	287.75	70.76	284.49
11-Sep-13	CCS 1	287.92	70.90	284.85
11-Sep-13	CCS 1	287.62	70.86	284.78
15-Sep-13	CCS 1	286.76	70.38	282.28
15-Sep-13	CCS 1	288.12	70.84	284.26
15-Sep-13	CCS 1	288.41	70.97	285.12
15-Sep-13	CCS 1	290.00	71.65	287.59
12-Sep-13	CCS 1	286.46	70.32	282.97
12-Sep-13	CCS 1	285.50	70.13	281.70
12-Sep-13	CCS 1	287.56	70.74	284.64
12-Sep-13	CCS 1	288.23	70.95	285.15
13-Sep-13	CCS 1	286.73	70.45	282.89
13-Sep-13	CCS 1	286.03	70.26	281.86
13-Sep-13	CCS 1	288.20	70.94	284.91
13-Sep-13	CCS 1	287.91	70.98	284.81
14-Sep-13	CCS 1	286.39	70.35	282.47
14-Sep-13	CCS 1	287.35	70.51	283.34
14-Sep-13	CCS 1	287.87	70.84	284.84
14-Sep-13	CCS 1	288.76	71.14	285.41

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 1	300.26	75.06	300.26

	Measured CCS	Chloride	Nitrate	Sulphate
23-Sep-13	CCS 1	299.43	74.66	298.71
23-Sep-13	CCS 1	299.42	74.57	298.92
23-Sep-13	CCS 1	299.66	74.83	299.15
23-Sep-13	CCS 1	299.21	74.59	298.63
23-Sep-13	CCS 1	300.72	74.89	300.23
23-Sep-13	CCS 1	300.43	74.85	299.57
23-Sep-13	CCS 1	297.83	73.54	295.35
23-Sep-13	CCS 1	297.87	73.53	294.90
25-Sep-13	CCS 1	304.16	74.73	298.24
25-Sep-13	CCS 1	303.60	74.61	297.71
25-Sep-13	CCS 1	297.91	73.58	295.00
25-Sep-13	CCS 1	298.35	73.66	294.59

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 1	292.63	73.16	292.63

	Measured CCS	Chloride	Nitrate	Sulphate
11-Oct-13	CCS 1	292.60	73.20	292.43
11-Oct-13	CCS 1	292.88	73.24	292.81
11-Oct-13	CCS 1	292.19	73.08	291.99
11-Oct-13	CCS 1	291.52	72.91	291.87
12-Oct-13	CCS 1	291.53	72.99	292.70
12-Oct-13	CCS 1	292.21	73.15	291.82
12-Oct-13	CCS 1	292.99	73.25	292.30
12-Oct-13	CCS 1	293.02	73.30	293.30
13-Oct-13	CCS 1	292.10	73.20	292.17
13-Oct-13	CCS 1	292.79	73.21	292.66
13-Oct-13	CCS 1	289.72	72.68	290.27
13-Oct-13	CCS 1	291.71	72.86	292.30
14-Oct-13	CCS 1	291.08	72.94	291.50
14-Oct-13	CCS 1	292.73	73.39	292.51
14-Oct-13	CCS 1	291.85	73.05	292.41
14-Oct-13	CCS 1	292.85	73.25	292.61
15-Oct-13	CCS 1	290.96	72.91	291.18
15-Oct-13	CCS 1	292.69	73.41	292.31
15-Oct-13	CCS 1	292.84	73.35	293.11
15-Oct-13	CCS 1	294.01	73.57	294.21
17-Oct-13	CCS 1	294.41	73.72	294.94
17-Oct-13	CCS 1	293.01	73.46	293.64
17-Oct-13	CCS 1	293.78	73.56	293.42
17-Oct-13	CCS 1	294.84	73.79	294.72
18-Oct-13	CCS 1	293.46	73.59	293.66
18-Oct-13	CCS 1	294.11	73.74	294.03
18-Oct-13	CCS 1	293.93	73.75	295.04
18-Oct-13	CCS 1	295.54	73.98	295.23
19-Oct-13	CCS 1	293.05	73.49	293.02
19-Oct-13	CCS 1	293.36	73.57	293.04
19-Oct-13	CCS 1	294.73	73.96	295.99
19-Oct-13	CCS 1	295.04	73.92	295.32

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 1	124.70	31.17	124.70

	Measured CCS	Chloride	Nitrate	Sulphate
04-Nov-13	CCS 1	122.34	29.89	119.51
04-Nov-13	CCS 1	122.52	29.91	119.55
04-Nov-13	CCS 1	123.98	30.49	120.85
04-Nov-13	CCS 1	121.91	29.96	120.74
05-Nov-13	CCS 1	122.05	29.97	121.12
05-Nov-13	CCS 1	121.79	29.79	118.25
06-Nov-13	CCS 1	122.13	29.96	118.89
06-Nov-13	CCS 1	122.20	29.99	118.95
06-Nov-13	CCS 1	122.13	29.96	118.89
06-Nov-13	CCS 1	122.20	29.99	118.95
07-Nov-13	CCS 1	122.93	30.05	120.15
07-Nov-13	CCS 1	122.82	30.03	120.11
07-Nov-13	CCS 1	122.44	30.00	119.39
07-Nov-13	CCS 1	122.20	29.94	118.33
08-Nov-13	CCS 1	122.04	29.92	118.81
08-Nov-13	CCS 1	122.35	29.95	118.62
12-Nov-13	CCS 1	122.27	29.91	119.97
12-Nov-13	CCS 1	121.88	29.80	119.54
08-Nov-13	CCS 1	122.52	30.04	120.55
08-Nov-13	CCS 1	122.93	30.03	121.09
08-Nov-13	CCS 1	123.89	30.44	122.04
13-Nov-13	CCS 1	121.69	29.84	119.78
13-Nov-13	CCS 1	122.71	30.00	119.30
14-Nov-13	CCS 1	120.74	29.27	117.30
14-Nov-13	CCS 1	121.35	29.46	117.48
15-Nov-13	CCS 1	122.14	29.83	119.49
15-Nov-13	CCS 1	122.46	30.02	119.56
15-Nov-13	CCS 1	122.31	29.90	119.70

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 1	130.36	32.59	130.36

	Measured CCS	Chloride	Nitrate	Sulphate
24-Oct-13	CCS 1	128.24	31.32	124.95
24-Oct-13	CCS 1	128.33	31.38	125.08
25-Oct-13	CCS 1	128.62	31.48	125.94
24-Oct-13	CCS 1	128.32	31.54	126.56
24-Oct-13	CCS 1	128.50	31.65	126.83
28-Oct-13	CCS 1	128.86	31.51	125.39
28-Oct-13	CCS 1	129.06	31.49	125.01
29-Oct-13	CCS 1	128.76	31.50	125.75
29-Oct-13	CCS 1	129.32	31.61	125.58
25-Oct-13	CCS 1	128.79	31.74	126.82
28-Oct-13	CCS 1	129.57	31.80	126.92
28-Oct-13	CCS 1	129.28	31.73	125.18
29-Oct-13	CCS 1	129.15	31.74	125.65
29-Oct-13	CCS 1	129.31	31.68	125.40
30-Oct-13	CCS 1	129.69	31.86	125.80
30-Oct-13	CCS 1	129.55	31.81	125.73

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 1	112.69	28.17	112.69

	Measured CCS	Chloride	Nitrate	Sulphate
19-Nov-13	CCS 1	110.49	26.94	107.14
19-Nov-13	CCS 1	110.09	26.91	107.39
19-Nov-13	CCS 1	110.49	27.13	108.70
19-Nov-13	CCS 1	110.70	27.15	109.28
20-Nov-13	CCS 1	110.83	27.04	107.49
20-Nov-13	CCS 1	110.90	27.09	107.10
20-Nov-13	CCS 1	110.73	27.16	109.01
20-Nov-13	CCS 1	111.01	27.18	107.78
21-Nov-13	CCS 1	110.62	27.13	108.00
21-Nov-13	CCS 1	110.58	27.00	107.14
22-Nov-13	CCS 1	110.39	27.09	106.85
22-Nov-13	CCS 1	110.78	27.10	107.49
26-Nov-13	CCS 1	110.67	27.19	108.77
27-Nov-13	CCS 1	110.61	27.14	109.22
27-Nov-13	CCS 1	110.57	27.18	108.68
27-Nov-13	CCS 1	110.47	27.04	107.36
28-Nov-13	CCS 1	110.56	27.10	108.48
28-Nov-13	CCS 1	110.68	27.18	108.28
29-Nov-13	CCS 1	110.74	27.18	108.69
29-Nov-13	CCS 1	110.61	27.07	108.10

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 1	124.70	31.17	124.70

	Measured CCS	Chloride	Nitrate	Sulphate
12-Nov-13	CCS 1	122.27	29.91	119.97
12-Nov-13	CCS 1	121.88	29.80	119.54
08-Nov-13	CCS 1	122.52	30.04	120.55
08-Nov-13	CCS 1	122.93	30.03	121.09
08-Nov-13	CCS 1	123.89	30.44	122.04
13-Nov-13	CCS 1	121.69	29.84	119.78
13-Nov-13	CCS 1	122.71	30.00	119.30
14-Nov-13	CCS 1	120.74	29.27	117.30
14-Nov-13	CCS 1	121.35	29.46	117.48
15-Nov-13	CCS 1	122.14	29.83	119.49
15-Nov-13	CCS 1	122.46	30.02	119.56
15-Nov-13	CCS 1	122.31	29.90	119.70
16-Nov-13	CCS 1	122.41	29.97	119.80
16-Nov-13	CCS 1	123.06	30.09	120.22

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 2	4.59	1.15	4.59

Date	Measured CCS	Chloride	Nitrate	Sulphate
09-Sep-13	CCS 2	4.57	1.12	4.52
11-Sep-13	CCS 2	4.48	1.14	4.32
11-Oct-13	CCS 2	4.43	1.10	3.84
11-Oct-13	CCS 2	4.48	1.11	4.07
12-Oct-13	CCS 2	4.50	1.15	4.99
12-Oct-13	CCS 2	4.54	1.12	3.83
12-Oct-13	CCS 2	4.58	1.11	4.47
12-Oct-13	CCS 2	4.48	1.11	4.28
13-Sep-13	CCS 2	4.42	1.12	3.80
13-Sep-13	CCS 2	4.57	1.13	4.51
13-Oct-13	CCS 2	4.50	1.14	4.95
13-Oct-13	CCS 2	4.45	1.13	4.31
14-Oct-13	CCS 2	4.57	1.13	4.24
14-Oct-13	CCS 2	4.41	1.10	3.22
14-Oct-13	CCS 2	4.50	1.15	4.52
14-Oct-13	CCS 2	4.51	1.09	3.89
15-Oct-13	CCS 2	4.47	1.12	3.46
15-Oct-13	CCS 2	4.55	1.14	3.60
17-Oct-13	CCS 2	4.64	1.18	5.74
17-Sep-13	CCS 2	4.50	1.14	4.14
17-Oct-13	CCS 2	4.55	1.13	4.31
17-Oct-13	CCS 2	4.65	1.16	5.12
18-Oct-13	CCS 2	4.64	1.11	3.25
18-Oct-13	CCS 2	4.70	1.12	3.18
18-Oct-13	CCS 2	4.84	1.19	5.91
18-Oct-13	CCS 2	4.82	1.15	4.80
19-Oct-13	CCS 2	4.67	1.12	3.90
19-Oct-13	CCS 2	4.64	1.12	3.52
19-Oct-13	CCS 2	4.85	1.20	5.91
19-Oct-13	CCS 2	4.81	1.19	5.94

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 2	4.76	1.19	4.76

	Measured CCS	Chloride	Nitrate	Sulphate
04-Nov-13	CCS 2	4.61	1.16	4.64
04-Nov-13	CCS 2	4.57	1.16	4.71
04-Nov-13	CCS 2	4.71	1.19	4.85
04-Nov-13	CCS 2	4.69	1.20	5.10
05-Nov-13	CCS 2	4.68	1.19	5.14
05-Nov-13	CCS 2	4.53	1.14	3.78
06-Nov-13	CCS 2	4.58	1.16	4.30
06-Nov-13	CCS 2	4.52	1.14	3.78
06-Nov-13	CCS 2	4.58	1.16	4.30
06-Nov-13	CCS 2	4.52	1.14	3.78
07-Nov-13	CCS 2	4.61	1.17	4.79
07-Nov-13	CCS 2	4.60	1.17	4.89
07-Nov-13	CCS 2	4.56	1.14	4.00
07-Nov-13	CCS 2	4.53	1.12	3.60
08-Nov-13	CCS 2	4.62	1.14	4.13
08-Nov-13	CCS 2	4.56	1.13	3.73
12-Nov-13	CCS 2	4.68	1.17	4.76
12-Nov-13	CCS 2	4.60	1.16	4.92
08-Nov-13	CCS 2	4.70	1.23	5.47
08-Nov-13	CCS 2	4.59	1.16	4.39
08-Nov-13	CCS 2	4.73	1.17	4.72
13-Nov-13	CCS 2	4.66	1.17	5.10
13-Nov-13	CCS 2	4.59	1.17	4.69
14-Nov-13	CCS 2	4.63	1.20	4.78
14-Nov-13	CCS 2	4.69	1.17	4.73
15-Nov-13	CCS 2	4.69	1.19	5.00
15-Nov-13	CCS 2	4.67	1.17	5.06
15-Nov-13	CCS 2	4.72	1.22	6.80
12-Nov-13	CCS 2	4.68	1.17	4.76
12-Nov-13	CCS 2	4.60	1.16	4.92
08-Nov-13	CCS 2	4.70	1.23	5.47
08-Nov-13	CCS 2	4.59	1.16	4.39
08-Nov-13	CCS 2	4.73	1.17	4.72
13-Nov-13	CCS 2	4.66	1.17	5.10
13-Nov-13	CCS 2	4.59	1.17	4.69
14-Nov-13	CCS 2	4.63	1.20	4.78
14-Nov-13	CCS 2	4.69	1.17	4.73

15-Nov-13	CCS 2	4.69	1.19	5.00
15-Nov-13	CCS 2	4.67	1.17	5.06
15-Nov-13	CCS 2	4.72	1.22	6.80
16-Nov-13	CCS 2	4.71	1.21	5.14
16-Nov-13	CCS 2	4.75	1.18	5.10

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 2	4.57	1.14	4.57

	Measured CCS	Chloride	Nitrate	Sulphate
24-Oct-13	CCS 2	4.47	1.12	4.73
24-Oct-13	CCS 2	4.47	1.12	4.73
25-Oct-13	CCS 2	4.39	1.11	4.14
24-Oct-13	CCS 2	4.52	1.14	4.92
24-Oct-13	CCS 2	4.42	1.13	4.78
28-Oct-13	CCS 2	4.49	1.15	3.93
28-Oct-13	CCS 2	4.34	1.11	3.50
29-Oct-13	CCS 2	4.48	1.13	4.52
25-Oct-13	CCS 2	4.53	1.14	4.98
28-Oct-13	CCS 2	4.48	1.14	4.67
28-Oct-13	CCS 2	4.40	1.08	3.48
29-Oct-13	CCS 2	4.40	1.11	3.82
29-Oct-13	CCS 2	4.40	1.08	3.58
30-Oct-13	CCS 2	4.35	1.09	3.31
30-Oct-13	CCS 2	4.46	1.09	3.56

Calculated CCS	Chloride	Nitrate	Sulphate
CCS 2	4.72	1.18	4.72

	Measured CCS	Chloride	Nitrate	Sulphate
19-Nov-13	CCS 2	4.52	1.13	4.36
19-Nov-13	CCS 2	4.66	1.15	4.61
19-Nov-13	CCS 2	4.73	1.18	5.12
19-Nov-13	CCS 2	4.73	1.17	5.33
20-Nov-13	CCS 2	4.67	1.15	4.44
20-Nov-13	CCS 2	4.62	1.12	3.94
20-Nov-13	CCS 2	4.79	1.20	5.19
20-Nov-13	CCS 2	4.58	1.13	4.33
21-Nov-13	CCS 2	4.67	1.17	4.75
21-Nov-13	CCS 2	4.87	1.11	3.96
22-Nov-13	CCS 2	4.64	1.14	4.25
22-Nov-13	CCS 2	4.63	1.13	4.19
26-Nov-13	CCS 2	4.75	1.21	5.34
27-Nov-13	CCS 2	4.72	1.22	5.41
27-Nov-13	CCS 2	4.68	1.21	5.20
27-Nov-13	CCS 2	4.57	1.13	4.58
28-Nov-13	CCS 2	4.69	1.17	5.02
28-Nov-13	CCS 2	4.67	1.18	4.92
29-Nov-13	CCS 2	4.66	1.21	5.07
29-Nov-13	CCS 2	4.65	1.17	4.87

OES

		MDL								
Duplicates		0.004	0.02	0.0003	0.001	0.004	0.003	0.004	0.02	0.004
Date	**Sample ID**	**As**	**Ca**	**Cd**	**K**	**Mg**	**Na**	**P**	**S**	**Se**
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
15-Aug-13	12331		58.55	0.0004	1.31	22.28	2.61		30.40	0.0221
15-Aug-13	12331-R		59.52	0.0004	1.27	22.20	2.51		30.52	0.0224
15-Aug-13	12903		45.01		0.57	15.89	1.08		15.80	0.0102
15-Aug-13	12903-R		44.81		0.57	15.88	1.06		15.81	0.0109
30-Sep-13	19246		158.35	0.0017	2.31	86.59	1.79		150.02	0.2174
30-Sep-13	19246-R		159.35	0.0017	2.27	86.30	1.75		149.41	0.2188
30-Sep-13	19326		11.03		0.40	3.51	0.21		0.62	
30-Sep-13	19326-R		11.16		0.40	3.53	0.21		0.62	
30-Sep-13	12904		26.34		0.83	8.79	0.75		2.14	
30-Aug-13	12904-R		26.31		0.84	8.97	0.77		2.16	
30-Aug-13	19615		137.08		1.96	65.59	2.60		145.25	0.0199
30-Aug-13	19615-R		135.71		1.98	65.33	2.62		144.28	0.0193
30-Aug-13	12085		104.80	0.0008	1.60	40.14	4.41		70.47	0.0687
30-Aug-13	12085-R		103.38	0.0008	1.64	40.41	4.51		70.81	0.0682
19-Aug-13	L32124		59.15		4.43	25.27	0.79	0.0066	75.89	0.0084
19-Aug-13	L32124-R		59.34		4.41	24.89	0.77	0.0293	75.09	0.0086
19-Aug-13	L32131		45.98		5.88	22.03	0.99	0.0251	57.39	0.0372
19-Aug-13	L32131-R		45.71		5.94	22.12	0.99	0.0075	57.50	0.0377
19-Aug-13	L32140		18.60		4.41	12.14	0.62	0.0104	19.74	0.0272
19-Aug-13	L32140-R		18.29		4.41	12.23	0.63	0.0111	19.89	0.0282
19-Aug-13	L32149		8.07		4.85	5.28	0.98	0.0141	10.99	0.0739
19-Aug-13	L32149-R	0.0054	8.13		4.82	5.32	0.97	0.0154	11.09	0.0736
19-Aug-13	L32158		14.24		4.06	5.90	0.65	0.0127	8.10	0.0185
19-Aug-13	L32158-R		14.60		4.08	5.88	0.65	0.0122	8.07	0.0176
15-Aug-13	L32064		18.23	0.0013	3.60	8.94	0.69		16.60	0.0168
15-Aug-13	L32064 R		17.85	0.0012	3.66	9.17	0.70		16.92	0.0165
15-Aug-13	L32080 LT3		14.41	0.0015	3.04	6.45	0.35		8.11	0.0102
15-Aug-13	L32080 LT3 R		14.56	0.0015	3.03	6.44	0.36		8.03	0.0112
15-Aug-13	L32108		17.51	0.0015	4.93	11.36	0.78		20.78	0.0177
15-Aug-13	L32108 R		17.56	0.0015	4.91	11.43	0.77		20.86	0.0164
15-Aug-13	L32113		18.53	0.0014	2.72	9.38	0.67		15.55	0.0131
15-Aug-13	L32113 R		18.43	0.0014	2.72	9.29	0.67		15.40	0.0123
06-Sep-13	L32218		15.85		3.60	3.36	2.36		6.88	0.0078
06-Sep-13	L32218-R		15.69		3.56	3.37	2.32		6.91	0.0097
06-Sep-13	L32224-DUP-1		47.38		2.60	7.09	2.84	0.1497	3.50	
06-Sep-13	L32224-DUP-1-R		45.20		2.63	7.15	2.87	0.1484	3.53	

06-Sep-13	L32233		54.50		3.94	12.49	1.70		54.11	
06-Sep-13	L32233-R		54.79		3.94	12.36	1.71		53.74	0.0024
06-Sep-13	L32242-crushed		10.69		5.33	2.73	20.56	0.0052	14.38	0.0164
06-Sep-13	L32242-crushed-R		10.86		5.16	2.70	19.99	0.0043	14.25	0.0162
05-Sep-13	10633	0.0043	98.31		0.74	25.54	2.04	0.0247	13.53	0.0212
05-Sep-13	10633-R	0.0053	97.09		0.73	25.33	2.03	0.0225	13.45	0.0192
05-Sep-13	L30696		41.61		5.28	21.09	1.78		54.14	0.0241
05-Sep-13	L30696-R		42.06		5.25	21.25	1.77		54.38	0.0236
05-Sep-13	L30706		35.78		7.18	7.78	2.86	0.0075	36.02	0.0907
05-Sep-13	L30706-R		35.48		7.19	7.74	2.87	0.0067	36.01	0.0881
05-Sep-13	L30716		17.79		6.77	5.97	2.03	0.0055	15.56	0.0504
05-Sep-13	L30716-R		17.75		6.82	6.01	2.03	0.0043	15.75	0.0511
05-Sep-13	L30732		38.19		6.74	9.59	2.24	0.0045	38.80	0.0505
05-Sep-13	L30732-R		38.44		6.62	9.55	2.21		38.64	0.0497
05-Sep-13	L30751		63.97	0.0005	3.88	25.20	0.40	0.0046	80.23	0.0118
05-Sep-13	L30751-R		65.56	0.0006	3.65	24.75	0.36		79.95	0.0128
04-Sep-13	C32264		32.10		5.81	17.39	394.90	0.0066	152.50	0.1761
04-Sep-13	C32264-R		31.76		5.92	17.54	390.48	0.0071	154.33	0.1758
04-Sep-13	C32268		22.45		4.17	13.47		0.0061	186.89	0.0446
04-Sep-13	C32268-R		22.28		4.21	13.56			188.44	0.0437
04-Sep-13	L32277		4.51		1.60	1.75	45.13	0.0065	28.46	0.0319
04-Sep-13	L32277-R		4.46		1.62	1.77	45.28	0.0056	28.39	0.0326
04-Sep-13	L32287	0.0053	2.44		0.95	0.37	45.48	0.0510	22.71	0.0150
04-Sep-13	L32287-R	0.0056	2.42		0.94	0.36	45.02	0.0510	22.40	0.0143
04-Sep-13	L32296	0.0235	0.67		2.18	0.27		0.0373	22.24	0.0380
04-Sep-13	L32296-R	0.0235	0.67		2.21	0.28		0.0343	22.25	0.0379
08-Sep-13	10686		298.93	0.0004	3.60	219.15	4.99	0.0222	418.49	0.2468
08-Sep-13	10686-R	0.0005	301.69	0.0004	3.65	219.69	5.03	0.0225	418.56	0.2499
08-Sep-13	L30357	0.0002	16.50		1.52	5.54	0.28	0.0057	13.82	0.0375
08-Sep-13	L30357-R		16.72		1.55	5.62	0.28	0.0063	14.09	0.0372
08-Sep-13	11143	0.0005	149.69	0.0000	3.14	57.45	4.08	0.0084	93.83	0.0340
08-Sep-13	11143-R		149.18		3.02	58.18	3.95	0.0080	94.79	0.0344
08-Sep-13	10667		98.60		0.82	31.06	1.64	0.0035	39.44	0.0573
08-Sep-13	10667-R		100.00		0.88	32.07	1.76	0.0028	40.72	0.0578
08-Sep-13	19455		110.39	0.0001	1.73	51.90	5.12	0.0044	87.21	0.0896
08-Sep-13	19455-R		109.99		1.74	51.93	5.10	0.0320	87.63	0.0918
08-Sep-13	19538	0.0004	206.06		2.80	133.06	6.23	0.0083	271.44	0.3421
08-Sep-13	19538-R		214.47		2.92	137.46	6.48	0.0072	281.20	0.3508
12-Sep-13	19556		53.96		0.52	17.32	1.77	0.0081	2.39	0.0015
12-Sep-13	19556-R		52.43		0.52	16.90	1.75	0.0076	2.33	0.0013
12-Sep-13	10686		298.93	0.0004	3.60	219.15	4.99	0.0222	418.49	0.2468
12-Sep-13	10686-R	0.0005	301.69	0.0004	3.65	219.69	5.03	0.0225	418.56	0.2499

12-Sep-13	19603	0.0009	36.04		0.37	14.97	0.61	0.0106	2.63	0.0006
12-Sep-13	19603-R	0.0010	36.15		0.37	14.92	0.61	0.0098	2.64	0.0006
12-Sep-13	19372	0.0008	189.31	0.0023	1.94	94.38	1.23	0.0062	171.13	0.2458
12-Sep-13	19372-R	0.0015	187.68	0.0023	1.99	95.16	1.26	0.0059	172.54	0.2474
12-Sep-13	374	0.0014	33.67		1.01	11.51	0.39	0.0240	2.87	0.0011
12-Sep-13	374-R	0.0016	33.47		0.99	11.57	0.38	0.0222	2.84	0.0008

Blind Duplicates										
Date	**Sample ID**	**As**	**Ca**	**Cd**	**K**	**Mg**	**Na**	**P**	**S**	**Se**
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
22-Aug-13	BD July 23		51.50		7.95	18.62	1.18	0.0062	40.41	0.1613
22-Aug-13	L01024		51.64		7.80	18.61	1.14	0.0064	40.08	0.1575
22-Aug-13	BD July 24		16.62		7.80	4.40	2.36	0.0099	6.90	0.0490
22-Aug-13	L01051-2		17.15		7.78	4.38	2.41	0.0209	7.03	0.0526
26-Aug-13	BD July 26		39.95		7.77	12.85	1.14	0.0073	19.39	0.0827
26-Aug-13	L01063		38.99		7.96	12.72	1.16	0.0067	19.40	0.0808
03-Sep-13	BD Aug 13		59.74		5.81	16.28	13.19	0.0083	65.12	0.0646
03-Sep-13	L30691		58.77		5.48	15.93	12.56	0.0055	64.99	0.0625
03-Sep-13	BD Aug 14		25.19		8.63	6.11	3.25	0.0143	19.93	0.0309
03-Sep-13	L30734		24.79		8.52	6.07	3.17	0.0124	19.74	0.0295
03-Sep-13	BD Aug 21		50.51		2.88	13.33	0.35	0.0047	51.09	0.0171
03-Sep-13	L30754		49.30		2.82	12.93	0.34	0.0044	49.15	0.0159
03-Sep-13	BD Aug 26	0.0052	22.04	0.0003	2.44	5.48	0.33	0.0141	14.46	0.0164
03-Sep-13	L30760		19.81		2.45	5.57	0.31	0.0068	13.26	0.0122
03-Sep-13	BD Aug 27		83.82	0.0003	3.35	17.11	0.63	0.0111	88.38	0.0377
03-Sep-13	L30766		76.83		3.43	17.29	0.65	0.0116	81.50	0.0307
13-Sep-13	BD Aug 28		70.73		2.63	31.56	0.76	0.0045	94.75	0.0607
13-Sep-13	L30773		66.85		2.58	31.33	0.71	0.0116	87.26	0.0474
13-Sep-13	BD Sep 3		95.14		4.94	28.07	0.57	0.0049	114.30	0.0402
13-Sep-13	L30774		94.21		5.02	28.53	0.58		113.43	0.0387
13-Sep-13	BDSep 5,2013		121.10	0.0003	6.10	36.27	0.54		146.85	0.0554
13-Sep-13	L30779		121.88		5.99	36.40	0.51		145.79	0.0545
17-Sep-13	BD SEPT 9		154.49	0.0029	10.50	49.61	3.32	0.1160	220.55	
17-Sep-13	L30788		157.82	0.0029	10.25	48.88	3.24	0.1152	216.38	
17-Sep-13	BD SEPT 10		18.06		9.11	2.83	6.30	0.0127	9.42	0.0119
17-Sep-13	L30742		18.45		8.80	2.80	6.09	0.0149	9.31	0.0111
18-Sep-13	BD SEPT 13	0.0054	1.76		2.33	0.67	36.02	0.0134	10.40	0.0184
18-Sep-13	L30625	0.0060	1.71		2.22	0.66	35.51	0.0145	10.18	0.0166
04-Oct-13	BD SEPT 16, 2013	0.0068	2.12		2.96	0.72	41.35	0.0358	12.56	0.0156
04-Oct-13	L30627	0.0062	2.09		2.89	0.70	40.60	0.0427	12.30	0.0143
04-Oct-13	BD SEPT 17, 2013	0.0197	0.57		2.54	0.22	94.75	0.0507	22.78	0.0469
04-Oct-13	L30633	0.0204	0.57		2.45	0.20	95.57	0.0629	22.76	0.0474
04-Oct-13	BD SEPT 23, 2013		1.17		1.21	0.35	89.84	0.0190	22.88	0.0482
04-Oct-13	L30635		1.01		1.17	0.33	90.78	0.0142	22.52	0.0488
04-Oct-13	BD SEPT 24, 2013		4.01		1.97	1.42	73.35	0.0155	25.68	0.0193

04-Oct-13	L30639		3.91		1.91	1.40	72.63	0.0132	24.90	0.0186
04-Oct-13	BD SEPT 26, 2013		8.91		1.83	2.83	63.54	0.0090	16.94	0.0305
04-Oct-13	L30643		8.75		1.83	2.79	62.93	0.0080	16.28	0.0303
04-Oct-13	BD Set30		12.81		1.25	6.13	0.31	0.0368	4.81	0.0126
04-Oct-13	L30348		12.66		1.25	6.02	0.31	0.0373	4.70	0.0115

Calibration Control Standards										
	Calculated CCS	**As**	**Ca**	**Cd**	**K**	**Mg**	**Na**	**P**	**S**	**Se**
	1:20 control mix	0.0500	5.00	0.0500	0.50	5.00	0.50	0.0500	5.00	0.0500
Date	**Measured CCS**	**As**	**Ca**	**Cd**	**K**	**Mg**	**Na**	**P**	**S**	**Se**
01-Oct-13	1:20 control mix	0.0541	5.18	0.0530	0.54	4.98	0.54	0.0524	5.07	0.0502
01-Oct-13	1:20 control mix	0.0531	5.11	0.0516	0.53	4.91	0.51	0.0521	5.01	0.0509
01-Sep-13	1:20 control mix	0.0525	5.14	0.0520	0.52	4.95	0.52	0.0506	5.14	0.0515
01-Sep-13	1:20 control mix	0.0532	5.16	0.0522	0.49	4.77	0.49	0.0482	5.11	0.0518
01-Oct-13	1:20 control mix	0.0494	4.95	0.0496	0.55	5.01	0.51	0.0526	5.28	0.0533
01-Oct-13	1:20 control mix	0.0518	5.14	0.0523	0.54	4.93	0.51	0.0525	5.19	0.0526
01-Sep-04	1:20 control mix	0.0516	5.08	0.0519	0.54	4.96	0.53	0.0521	5.08	0.0510
01-Sep-04	1:20 control mix	0.0517	5.10	0.0522	0.52	4.91		0.0510	5.06	0.0504
01-Sep-04	1:20 control mix	0.0503	5.10	0.0509	0.55	4.96	0.54	0.0495	5.08	0.0514
01-Oct-04	1:20 control mix	0.0529	5.18	0.0514	0.55	5.01	0.52	0.0526	5.25	0.0529
01-Oct-04	1:20 control mix	0.0524	5.06	0.0514	0.54	4.88	0.51	0.0510	4.99	0.0515
01-Sep-06	1:20 control mix	0.0503	5.10	0.0509	0.55	4.96	0.54	0.0495	5.08	0.0514
01-Sep-06	1:20 control mix	0.0521	5.30	0.0534	0.52	4.84	0.50	0.0514	5.13	0.0512
01-Oct-07	1:20 control mix	0.0525	5.25	0.0534	0.52	4.87	0.49	0.0515	5.04	0.0533
01-Oct-07	1:20 control mix	0.0520	4.99	0.0505	0.53	4.81	0.51	0.0511	4.93	0.0512
01-Oct-09	1:20 control mix	0.0515	5.04	0.0518	0.53	4.87	0.50	0.0515	4.93	0.0498
01-Oct-09	1:20 control mix	0.0531	5.09	0.0511	0.53	4.90	0.51	0.0522	5.04	0.0507
01-Sep-11	1:20 control mix	0.0522	5.03	0.0515	0.54	4.99	0.52	0.0515	5.18	0.0524
01-Aug-13	1:20 control mix	0.0531	4.92	0.0534	0.46	4.68	0.47	0.0539	5.38	0.0527
01-Sep-13	1:20 control mix	0.0527	5.19	0.0525	0.51	5.03	0.49	0.0549	5.23	0.0519
01-Sep-13	1:20 control mix	0.0529	5.09	0.0513	0.54	5.01	0.52	0.0527	5.22	0.0509
01-Aug-14	1:20 control mix	0.0541	5.25	0.0519	0.47	4.88	0.47	0.0507	5.18	0.0529
01-Aug-15	1:20 control mix	0.0546	5.20	0.0537	0.49	4.80	0.48	0.0536	5.23	0.0524
01-Aug-15	1:20 control mix	0.0547	5.19	0.0533	0.50	4.77	0.49	0.0531	5.23	0.0539
01-Aug-15	1:20 control mix	0.0530	5.26	0.0533	0.49	4.81	0.48	0.0544	5.35	0.0525
01-Oct-15	1:20 control mix	0.0520	5.09	0.0514	0.53	4.95	0.53	0.0521	5.09	0.0515
01-Sep-16	1:20 control mix	0.0522	5.10	0.0516	0.54	4.98	0.53	0.0534	5.11	0.0521
01-Sep-16	1:20 control mix	0.0514	5.10	0.0508	0.54	5.00	0.54	0.0529	5.16	0.0521
01-Oct-16	1:20 control mix	0.0528	5.17	0.0524	0.52	4.87	0.49	0.0535	5.01	0.0530
01-Oct-16	1:20 control mix	0.0521	5.06	0.0521	0.53	4.91	0.51	0.0541	5.02	0.0519
01-Sep-17	1:20 control mix	0.0530	5.24	0.0539	0.50	4.82	0.50	0.0525	5.06	0.0484
01-Sep-17	1:20 control mix	0.0509	5.11	0.0507	0.53	4.97	0.52	0.0530	5.18	0.0484
01-Sep-18	1:20 control mix	0.0515	5.15	0.0536	0.50	4.84	0.50	0.0513	5.06	0.0518
01-Sep-18	1:20 control mix	0.0523	5.10	0.0512	0.53	4.96	0.53	0.0539	5.12	0.0528
01-Sep-19	1:20 control mix	0.0534	5.05	0.0513	0.55	4.95	0.55	0.0546	5.14	0.0517

01-Sep-19	1:20 control mix	0.0544	5.16	0.0530	0.52	4.93	0.52	0.0537	5.18	0.0518
13-Sep-13	1:20 control mix	0.0527	5.19	0.0525	0.51	5.03	0.49	0.0549	5.23	0.0519
13-Sep-13	1:20 control mix	0.0529	5.09	0.0513	0.54	5.01	0.52	0.0527	5.22	0.0509
16-Sep-13	1:20 control mix	0.0522	5.10	0.0516	0.54	4.98	0.53	0.0534	5.11	0.0521
16-Sep-13	1:20 control mix	0.0514	5.10	0.0508	0.54	5.00	0.54	0.0529	5.16	0.0521
18-Sep-13	1:20 control mix	0.0515	5.15	0.0536	0.50	4.84	0.50	0.0513	5.06	0.0518
18-Sep-13	1:20 control mix	0.0523	5.10	0.0512	0.53	4.96	0.53	0.0539	5.12	0.0528
19-Sep-13	1:20 control mix	0.0534	5.05	0.0513	0.55	4.95	0.55	0.0546	5.14	0.0517
19-Sep-13	1:20 control mix	0.0544	5.16	0.0530	0.52	4.93	0.52	0.0537	5.18	0.0518
02-Oct-13	1:20 control mix	0.0528	5.30	0.0534	0.55	4.95	0.54	0.0511	5.19	0.0504
07-Oct-13	1:20 control mix	0.0525	5.25	0.0534	0.52	4.87	0.49	0.0515	5.04	0.0533
07-Oct-13	1:20 control mix	0.0520	4.99	0.0505	0.53	4.81	0.51	0.0511	4.93	0.0512
15-Oct-13	1:20 control mix	0.0520	5.09	0.0514	0.53	4.95	0.53	0.0521	5.09	0.0515
15-Oct-13	1:20 control mix	0.0520	5.15	0.0531	0.52	4.95	0.50	0.0532	5.07	0.0515
31-Oct-13	1:20 control mix	0.0541	5.18	0.0530	0.54	4.98	0.54	0.0524	5.07	0.0502
31-Oct-13	1:20 control mix	0.0531	5.11	0.0516	0.53	4.91	0.51	0.0521	5.01	0.0509
05-Dec-13	1:20 control mix	0.0491	5.03	0.0517	0.53	4.79	0.50	0.0503	4.67	0.0520
05-Dec-13	1:20 control mix	0.0515	5.06	0.0525	0.53	4.86	0.49	0.0510	4.84	0.0537
09-Dec-13	1:20 control mix	0.0521	5.13	0.0529	0.54	4.86	0.50	0.0520	4.54	0.0541
09-Dec-13	1:20 control mix	0.0514	5.06	0.0526	0.55	4.86	0.53	0.0522	4.64	0.0534
18-Dec-13	1:20control mix	0.0512	4.98	0.0516	0.53	4.89	0.49	0.0514	5.14	0.0487
18-Dec-13	1:20control mix	0.0513	5.02	0.0513	0.53	4.84	0.50	0.0511	5.08	0.0505

Calibration Control Standards										
	Calculated CCS	As	Ca	Cd	K	Mg	Na	P	S	Se
	1:10 control mix	0.1000	10.00	0.1000	1.00	10.00	1.00	0.1000	10.00	0.1000
01-Sep-19	1:10 control mix	0.1071	10.12	0.1047	1.09	9.80	1.04	0.1057	10.34	0.1032
01-Sep-19	1:10 control mix	0.1042	10.17	0.1073	1.04	9.57	1.00	0.1013	10.11	0.1005
01-Sep-18	1:10 control mix	0.1029	10.25	0.1062	0.99	9.42	0.96	0.0983	10.05	0.1005
01-Sep-18	1:10 control mix	0.1024	10.01	0.1022	1.05	9.77	1.01	0.1025	10.19	0.1024
01-Sep-17	1:10 control mix	0.1029	10.26	0.1076	0.98	9.40	0.96	0.1005	9.98	0.0965
01-Sep-17	1:10 control mix	0.1036	10.02	0.1010	1.06	9.91	1.03	0.1042	10.36	0.1002
01-Sep-16	1:10 control mix	0.1034	10.05	0.1037	1.11	9.82	1.11	0.1022	10.26	0.1033
01-Sep-16	1:10 control mix	0.1030	10.07	0.1009	1.09	9.72	1.08	0.1015	10.21	0.1029
01-Sep-13	1:10 control mix	0.1042	10.27	0.1047	1.05	9.84	1.03	0.1019	10.49	0.1036
01-Sep-13	1:10 control mix	0.1058	10.03	0.1078	1.06	10.23	1.03	0.1059	10.76	0.1064
01-Sep-11	1:10 control mix	0.1022	9.92	0.1009	1.07	9.71	1.03	0.0999	10.05	0.1012
01-Oct-31	1:10 control mix	0.1018	9.99	0.1022	1.03	9.47	1.02	0.1007	9.86	0.0969
01-Oct-31	1:10 control mix	0.1044	10.09	0.1031	1.04	9.32	1.01	0.1029	10.03	0.0999
01-Oct-16	1:10 control mix	0.1055	10.29	0.1063	1.04	9.64	1.01	0.1050	10.11	0.1010
01-Oct-16	1:10 control mix	0.1047	10.08	0.1039	1.04	9.65	1.01	0.1059	10.09	0.1024
01-Oct-15	1:10 control mix	0.1046	10.13	0.1026	1.06	9.74	1.01	0.1047	10.22	0.1027
01-Oct-09	1:10 control mix	0.1029	9.94	0.1047	1.03	9.43	0.99	0.1020	9.96	0.1011
01-Oct-09	1:10 control mix	0.1034	10.02	0.1010	1.07	9.61	1.02	0.1023	10.11	0.1007
01-Oct-07	1:10 control mix	0.1041	10.56	0.1063	1.03	9.57	1.01	0.1039	10.25	0.1045
01-Oct-07	1:10 control mix	0.1036	10.11	0.1030	1.08	9.66	1.06	0.1040	10.13	0.1032
01-Oct-04	1:10 control mix	0.1060	10.08	0.1020	1.09	9.81	1.06	0.1051	10.48	0.1044
01-Oct-04	1:10 control mix	0.1035	10.24	0.1011	1.07	9.53	1.04	0.1024	10.00	0.1001
01-Oct-03	1:10 control mix	0.1022	9.82	0.0997	1.10	9.73	1.05	0.1049	10.50	0.1042
01-Oct-03	1:10 control mix	0.1046	10.19	0.1044	1.07	9.75	1.03	0.1058	10.23	0.1044
01-Sep-06	1:10 control mix	0.1018	10.08	0.1028	1.05	9.66	1.00	0.0987	10.15	0.1032
01-Sep-06	1:10 control mix	0.1021	10.51	0.1071	1.00	9.45	0.98	0.0964	10.09	0.1009
01-Sep-03	1:10 control mix	0.1042	10.11	0.1001	1.04	9.73	0.99	0.1016	10.19	0.1027
01-Sep-03	1:10 control mix	0.1035	10.18	0.1030	0.98	9.33	0.95	0.0971	10.13	0.0995
01-Sep-04	1:10 control mix	0.1061	10.61	0.1047	1.10	9.92	1.06	0.1055	10.30	0.1021
01-Sep-04	1:10 control mix	0.1030	9.93	0.1025	1.06	9.70	1.05	0.1028	10.15	0.1008
01-Sep-04	1:10 control mix	0.1018	10.08	0.1028	1.05	9.66	1.00	0.0987	10.15	0.1032
01-Aug-15	1:10 control mix	0.1048	10.11	0.1041	1.03	9.58	0.99	0.1040	10.21	0.1030
01-Aug-15	1:10 control mix	0.1029	10.14	0.1021	1.03	9.59	0.99	0.1045	10.29	0.1048
01-Aug-14	1:10 control mix	0.1051	10.24	0.1041	1.01	9.62	0.98	0.1024	10.20	0.1029
01-Aug-13	1:10 control mix	0.1047	9.97	0.1043	1.05	9.58		0.1098	10.30	0.1024
13-Sep-13	1:10 control mix	0.1042	10.27	0.1047	1.05	9.84	1.03	0.1019	10.49	0.1036
13-Sep-13	1:10 control mix	0.1058	10.03	0.1078	1.06	10.23	1.03	0.1059	10.76	0.1064
16-Sep-13	1:10 control mix	0.1030	10.07	0.1009	1.09	9.72	1.08	0.1015	10.21	0.1029
16-Sep-13	1:10 control mix	0.1034	10.05	0.1037	1.11	9.82	1.11	0.1022	10.26	0.1033
18-Sep-13	1:10 control mix	0.1029	10.25	0.1062	0.99	9.42	0.96	0.0983	10.05	0.1005

18-Sep-13	1:10 control mix	0.1024	10.01	0.1022	1.05	9.77	1.01	0.1025	10.19	0.1024
19-Sep-13	1:10 control mix	0.1042	10.17	0.1073	1.04	9.57	1.00	0.1013	10.11	0.1005
19-Sep-13	1:10 control mix	0.1071	10.12	0.1047	1.09	9.80	1.04	0.1057	10.34	0.1032
02-Oct-13	1:10 control mix	0.1031	10.40	0.1055	1.06	9.65	1.05	0.1013	10.33	0.1000
07-Oct-13	1:10 control mix	0.1036	10.11	0.1030	1.08	9.66	1.06	0.1040	10.13	0.1032
07-Oct-13	1:10 control mix	0.1041	10.56	0.1063	1.03	9.57	1.01	0.1039	10.25	0.1045
15-Oct-13	1:10 control mix	0.1046	10.13	0.1026	1.06	9.74	1.01	0.1047	10.22	0.1027
15-Oct-13	1:10 control mix	0.1054	10.21	0.1047	1.03	9.84	0.99	0.1047	10.23	0.1008
31-Oct-13	1:10 control mix	0.1018	9.99	0.1022	1.03	9.47	1.02	0.1007	9.86	0.0969
31-Oct-13	1:10 control mix	0.1044	10.09	0.1031	1.04	9.32	1.01	0.1029	10.03	0.0999
05-Dec-13	1:10 control mix	0.1023	9.83	0.1006	1.07	9.47	1.02	0.0996	9.44	0.1022
05-Dec-13	1:10 control mix	0.1037	10.08	0.1024	1.06	9.48	1.00	0.1017	9.51	0.1047
09-Dec-13	1:10 control mix	0.1045	10.13	0.1047	1.11	9.75	1.09	0.1053	9.62	0.1071
09-Dec-13	1:10 control mix	0.1057	10.36	0.1049	1.08	9.58	1.04	0.1047	9.46	0.1036
18-Dec-13	1:10 control mix	0.1015	9.90	0.1021	1.02	9.34	0.97	0.1007	9.83	0.0995
18-Dec-13	1:10 control mix	0.1016	9.92	0.1032	1.03	9.35	0.99	0.0998	9.83	0.0983

Recovery

		As	Ca	Cd	K	Mg	Na	P	S	Se
	LFM	0.9306	0.87	0.9434	0.96	0.91	0.95	1.0064	1.06	1.1107
04-Oct-13	19429									
04-Oct-13	19429-F	0.9058		0.9132	0.83		0.94	1.0355		
04-Oct-13	19424									
04-Oct-13	19424-F	0.9710		0.9134	0.90		0.95	1.0160		
04-Oct-13	19486									
04-Oct-13	19486-F	1.0936	0.95	0.9526	0.79	0.91	0.98	0.9788	1.00	0.9045
04-Oct-13	L30336									
04-Oct-13	L30336-F	0.9564		0.9824	0.75		0.82	1.0182		
04-Oct-13	10687									
04-Oct-13	10687-F	1.0122	0.91	0.9590		0.89	0.92	0.9483	0.97	0.9134
07-Oct-13	L30358									
07-Oct-13	L30358-F	1.0236	0.78	0.9802	0.87	0.86	0.84	1.0025	1.01	1.0855
07-Oct-13	19337									
07-Oct-13	19337-F	1.0110	0.93	0.9772	0.88	0.89	0.91	0.9740	1.04	1.0670
07-Oct-13	12336									
07-Oct-13	12336-F			0.9568	0.76		0.80	1.0464		
07-Oct-13	19461									
07-Oct-13	19461-F	0.8804		0.9750	0.82		0.93	0.9827		
07-Oct-13	12682									
07-Oct-13	12682-F	1.0340	0.90	0.9412	0.92	0.88	0.94	0.9941	1.03	1.0521
07-Oct-13	12308									
07-Oct-13	12308-F			0.9344	0.82		1.00	1.0808		0.9983
07-Oct-13	11148									
07-Oct-13	11148-F		0.96	0.9730		0.97	0.96	1.0711	0.88	1.0702
14-Aug-13	L32125									
14-Aug-13	L32125-F		0.93	1.0114		0.93	0.93	1.0155	0.72	0.9565
14-Aug-13	L32132									
14-Aug-13	L32132-F		0.97	1.0538		0.93	0.96	0.9858	0.86	0.9599
14-Aug-13	L32141									
14-Aug-13	L32141-F	1.0022	1.04	1.0606	0.71	0.98	0.97	0.9654	1.04	0.9592
14-Aug-13	L32149-DUP									
14-Aug-13	L32149-DUP-F	1.0022	1.04		0.71	0.98	0.97		1.04	0.9592
14-Aug-13	L32149-DUP									
14-Aug-13	L32149-DUP-F		0.87	1.0014		0.96	0.94	0.9945	0.81	1.0003
15-Aug-13	L32065									
15-Aug-13	L32065 F		0.92		0.78	1.03	1.00	1.0089	1.00	1.1021
15-Aug-13	L32073									
15-Aug-13	L32073 F	1.0502	0.98	0.9884		0.96	0.95	1.0769	1.02	1.0117
15-Aug-13	L32100 LT2									
15-Aug-13	L32100 LT2 F		0.96	0.9666		0.96	0.96	0.9923	1.01	1.0276

15-Aug-13	L32109									
15-Aug-13	L32109 F		0.93	0.9650	0.76	0.97	0.96	0.9517	1.01	1.0701
15-Aug-13	L32114									
15-Aug-13	L32114 F	0.9110	0.96	0.9400	0.97	0.98	1.01	0.9119	1.05	1.1486
13-Aug-13	19325									
13-Aug-13	19325F	1.1474	0.77	0.9198	0.98	0.97	0.98	1.0514	1.06	1.1307
13-Aug-13	19342									
13-Aug-13	19342F	0.9126	0.99	0.9188	0.92	1.00		0.9932	1.01	1.0047
04-Sep-13	L32264									
04-Sep-13	L32264-F		0.99	0.9248	0.95	1.02		1.0241	0.92	0.9577
04-Sep-13	L32268									
04-Sep-13	L32268-F	0.9046	1.00	0.9348	0.90	0.98		0.9943	0.91	0.9923
04-Sep-13	L32287-DUP									
04-Sep-13	L32287-DUP-F		1.00	0.9546	0.94	1.01		1.0265	0.88	0.8827
04-Sep-13	L32278									
04-Sep-13	L32278-F		0.99	0.9442	0.85	0.99		1.0171	0.89	0.9998
04-Sep-13	L32296-DUP									
04-Sep-13	L32296-DUP-F	1.0516		1.0778	0.89	0.88	0.88	1.0534		1.0128
19-Sep-13	19561									
19-Sep-13	19561-F		0.97	1.0504	0.92	0.99	1.00	1.0046	1.09	1.1406
19-Sep-13	19594									
19-Sep-13	19594-F			1.0174	0.91	0.92	0.95	1.0620	0.90	1.0424
19-Sep-13	19585									
19-Sep-13	19585-F			0.9194	0.93	0.83	0.85			0.9592
19-Sep-13	19562									
19-Sep-13	19562-F			1.0974	0.88		1.02			
19-Sep-13	19544									
19-Sep-13	19544-F		1.04	1.0456	0.99	1.03	1.04	1.0750	1.11	1.1408
19-Sep-13	19567									
19-Sep-13	19567-F	1.0908		1.0404	0.91	0.92	0.91	1.0443	0.88	1.0944
19-Sep-13	19588									
19-Sep-13	19588-F	0.8696		0.9374	0.87		0.98	1.1494		
03-Oct-13	19629									
03-Oct-13	19629-F	1.0690		0.9234	1.00	0.88	0.98		1.01	
03-Oct-13	19557									
03-Oct-13	19557-F	0.9630		0.9172	0.93		1.05			
03-Oct-13	19408									
03-Oct-13	19408-F			0.9038	0.87		0.98	1.1309		
03-Oct-13	19632									
03-Oct-13	19632-F	0.9306	0.87	0.9434	0.96	0.91	0.95	1.0064	1.06	1.1107
04-Oct-13	19429									
04-Oct-13	19429-F	0.9058		0.9132	0.83		0.94	1.0355		
04-Oct-13	19424									

04-Oct-13	19424-F	0.9710		0.9134	0.90		0.95	1.0160		
04-Oct-13	19486									
04-Oct-13	19486-F	1.0764		0.9016	0.82		0.93	1.0040		
04-Oct-13	19483									
04-Oct-13	19483-F	1.0936	0.95	0.9526	0.79	0.91	0.98	0.9788	1.00	0.9045
04-Oct-13	L30336									
04-Oct-13	L30336-F	0.9746	0.95	0.9490	0.92	0.90	0.99	0.9386	1.03	1.0291
04-Oct-13	L30348									
04-Oct-13	L30348-F	0.9564		0.9824	0.75		0.82	1.0182		
04-Oct-13	10687									
04-Oct-13	10687-F	1.1444		0.9788	0.80		0.92	1.0422		
17-Sep-13	19370									
17-Sep-13	19370-F	0.9252	1.00	0.9908	0.86	1.01	1.01	1.0653	1.06	1.0481
17-Sep-13	L30757									
17-Sep-13	L30757-F	1.0520	0.83	0.9846	0.80	1.02	0.89	1.0633	0.81	1.0877
17-Sep-13	L30790									
17-Sep-13	L30790-F		0.98	1.0228	0.91	0.99	0.94	1.0413	1.09	1.1063
17-Sep-13	378									
17-Sep-13	378-F	1.0696		1.0644	0.80	0.91	0.79	1.0365	0.87	0.9605
17-Sep-13	12327									
17-Sep-13	12327-F	0.8552		1.0180	0.80		0.95	1.0754		
17-Sep-13	12268									
17-Sep-13	12268-F	1.1294		1.0572	0.82	0.77	0.93	1.0603		
17-Sep-13	19304									
17-Sep-13	19304-F	0.9876	0.95	0.9722	0.90	0.88	0.96	0.9226	0.97	0.9653
09-Oct-13	L30384(2)									
09-Oct-13	L30384(2)-F		0.89	0.9724		0.89	0.90	0.9526	0.95	0.9345
09-Oct-13	L30402									
09-Oct-13	L30402-F	1.0744	0.93	0.9980	0.85	0.90	0.93	0.9230	0.98	0.8988
09-Oct-13	L30438									
09-Oct-13	L30438-F		0.95	0.9862	0.88	0.91	0.97	1.0003	1.01	
15-Oct-13	L30439									
15-Oct-13	L30439-F			0.9776	0.80	0.78	0.96	0.9565		0.9559
15-Oct-13	11014									
15-Oct-13	11014-F	1.0982		0.9776	0.74		0.81	0.9694		0.9371
15-Oct-13	11052									
15-Oct-13	11052-F	0.8808		0.9460	0.80			0.9983		0.9534
15-Oct-13	11103									
15-Oct-13	11103-F	0.9282	0.94	0.9606	0.62	0.90	0.93	0.8777	0.99	0.9941
15-Oct-13	L30413									
15-Oct-13	L30413-F			0.8500		0.76		0.9909	0.82	1.0290
31-Oct-13	Fairview Domestic									

31-Oct-13	Fairview Domestic-F	1.0722	0.98	0.8688	1.02	0.92	1.04	1.0008	1.07	1.1253
31-Oct-13	11168									
31-Oct-13	11168-F	0.8990	0.94	0.9324		0.90	0.96	0.9460	0.99	0.9160
31-Oct-13	L30451									
31-Oct-13	L30451-F		0.97	0.9576	0.91	0.90		0.9666	0.93	0.9501
09-Dec-13	L30651									
09-Dec-13	L30651-F	0.8980	0.80	0.9558		0.89		0.9492		0.9978
09-Dec-13	L30661									
09-Dec-13	L30661-F	0.8830	0.99	0.9934	0.74	0.91		0.9443	0.94	0.9599
09-Dec-13	L30671									
09-Dec-13	L30671-F	0.9876	0.98	0.9016	0.94	0.91		1.0067	0.95	1.0057
09-Dec-13	BD Nov,18,13									
09-Dec-13	BD Nov,18,13-F	0.0070	30.95	0.0046	5.80	24.81	45.57	0.0650	51.12	0.0593

MS

		MDL								
Duplicates		0.0015	0.001	0.001	0.0015	0.005	0.0001	0.0005	0.00001	0.0001
Date	**Sample ID**	**Na**	**Mg**	**P**	**K**	**Ca**	**As**	**Se**	**Cd**	**Ba**
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
04/04/2013	EV-BRD-30585	44.87	750.55	0.06	92.15	931.42	0.0123	0.1175	0.00	0.06
04/04/2013	EV-BRD-30585R	44.58	771.08	0.05	90.26	940.67	0.0100	0.0981	0.00	0.06
24/07/2013	# 12905	0.89	9.69	0.03	0.75	25.23	0.0003		0.00	0.12
24/07/2013	# 12905R	0.87	9.70	0.03	0.77	26.03	0.0003		0.00	0.12
24/07/2013	# 19230	0.99	10.58	0.03	0.83	33.13	0.0002		0.00	0.13
24/07/2013	# 19230R	0.91	10.23	0.03	0.80	32.20	0.0003		0.00	0.13
24/07/2013	# 19246	2.41	102.50	0.01	2.50	218.93	0.0053	0.1726	0.00	0.02
24/07/2013	# 19246R	2.48	100.67	0.01	2.48	211.01	0.0048	0.1720	0.00	0.02
24/07/2013	# 19260	1.31	89.58	0.01	1.91	190.87	0.0045	0.1447	0.00	0.02
24/07/2013	# 19260R	1.31	86.61	0.01	1.90	192.59	0.0045	0.1445	0.00	0.02
14/03/2013	LC-LP #1	7.70	167.32	0.03	11.29	312.57	0.0059	0.0663	0.00	0.08
14/03/2013	LC-LP #1R	7.38	163.06	0.03	10.84	301.09	0.0046	0.0656	0.00	0.08
14/03/2013	LC-WLC-EXC 31008A	6.96	53.09	0.06	11.13	125.95	0.0111	0.1468	0.00	0.14
14/03/2013	LC-WLC-EXC 31008AR	7.15	54.42	0.06	11.46	127.87	0.0112	0.1537	0.00	0.14
26/02/2013	LC-WLC-12-07b L32036A	1.63	1.60	0.04	1.79	16.36	0.0006	0.0119	0.00	0.07
26/02/2013	LC-WLC-12-07b L32036AR	1.59	1.61	0.04	1.73	16.05	0.0005	0.0113	0.00	0.07
26/02/2013	CRO-B5-12-1b L32294A	99.08	0.44	0.07	0.57	1.17	0.0053	0.0332	ud	0.08
26/02/2013	CRO-B5-12-1b L32294AR	102.12	0.44	0.07	0.62	1.12	0.0061	0.0328	ud	0.09
12/02/2013	CRO-B5-12-02 L32257A	7.30	41.68	0.03	5.46	138.51	0.0029	0.0538	0.00	0.04
12/02/2013	CRO-B5-12-02 L32257AR	7.16	41.42	0.03	5.40	138.43	0.0006	0.0541	0.00	0.03
02/05/2013	32000A-LC-WLC-1209c	2.58	1.56	0.02	1.10	10.32	0.0007	0.0015	ud	0.01
02/05/2013	32000A-LC-WLC-1209cR	2.56	1.52	0.02	1.07	10.18	0.0005	0.0014	ud	0.01
02/05/2013	32017A-LC-WLC-1209c	2.26	2.26	0.04	0.92	13.88	0.0005		0.00	0.04
02/05/2013	32017A-LC-WLC-1209cR	2.23	2.26	0.04	0.95	14.36	0.0006		0.00	0.04
02/05/2013	C32044A-LC-WLC-1210c	4.14	35.25	0.03	2.35	89.49	0.0004	0.0217	0.00	0.09
02/05/2013	C32044A-LC-WLC-1210cR	3.97	35.51	0.02	2.30	90.81	0.0004	0.0228	0.00	0.09

02/05/2013	L30103A-LT3-LC-WLC-1205c	0.44	5.09	0.04	3.37	9.50		0.0044	0.00	0.15
02/05/2013	L30103A-LT3-LC-WLC-1205cR	0.57	5.13	0.04	3.25	9.49	0.0007	0.0038	0.00	0.16
02/05/2013	30714-CRO-CC3-1201	1.79	5.06	0.05	5.05	19.20	0.0016	0.0104	0.00	0.18
02/05/2013	30714-CRO-CC3-1201R	1.84	5.12	0.05	5.05	19.31	0.0012	0.0122	0.00	0.18
20/03/2013	LC-WLC-1205c L32080A	1.04	23.88	0.02	6.13	43.96	0.0008	0.0122	0.00106	0.03
20/03/2013	LC-WLC-1205c L32080AR	1.05	23.95	0.02	6.22	43.65	0.0007	0.0183	0.00118	0.03
22/05/2013	EV-BRD-12-02a L32204A Dup	0.47	4.70	0.03	4.51	11.32	0.0015	0.0134	0.00	0.16
22/05/2013	EV-BRD-12-02a L32204A DupR	0.48	4.76	0.03	4.50	11.56	0.0016	0.0118	0.00	0.16
22/05/2013	FRO-TCR-12-01 L30833A	1.31	2.65	0.03	7.46	6.97	0.0051	0.0512		0.26
22/05/2013	FRO-TCR-12-01 L30833AR	1.35	2.65	0.03	7.41	6.98	0.0041	0.0520		0.26
22/05/2013	LC-WLC-12-05c L30062LT4	0.21	3.75	0.06	1.87	6.29	0.0011	0.0091	0.00	0.08
22/05/2013	LC-WLC-12-05c L30062LT4R	0.20	3.71	0.05	1.84	6.12	0.0007	0.0141	0.00	0.08
22/05/2013	LC-WLC-12-10c L32041	1.20	2.02	0.05	1.31	12.88				0.03
22/05/2013	LC-WLC-12-10c L32041R	1.24	2.08	0.05	1.33	13.05	0.0001		0.00	0.03
22/05/2013	EV-BRD-12-02a L32191AD	1.07	13.08	0.05	6.44	32.04	0.0017	0.0362	0.00	0.05
22/05/2013	EV-BRD-12-02a L32191ADR	1.05	13.05	0.05	6.50	32.39	0.0025	0.0421	0.00	0.05
22/05/2013	12-02a 30381-20 MPa	8.04	149.88	0.14	7.59	286.94	0.0030	0.0363	0.00	0.05
22/05/2013	12-02a 30381-20 MPaR	7.25	151.22	0.13	6.94	284.93	0.0018	0.0374	0.00	0.05
01/06/2013	30382-30MPa	33.52	276.61	0.31	7.06	246.67	0.0116	0.0710	0.01	0.06
01/06/2013	30382-30MPaR	35.77	281.00	0.30	7.42	239.83	0.0089	0.0771	0.01	0.06
01/06/2013	# 10464	7.34	171.07	0.04	4.21	309.81	0.0277	0.3777	0.00	0.03
01/06/2013	# 10464R	7.40	173.61	0.04	4.20	311.24	0.0225	0.3745	0.00	0.03
01/06/2013	FRO-TCR-12-02 L30807A	5.12	2.46	0.04	13.34	7.19	0.0055	0.0275	0.00	1.04
01/06/2013	FRO-TCR-12-02 L30807AR	5.16	2.40	0.04	13.31	7.18	0.0054	0.0279	0.00	1.05
28/05/2013	FRO-TCR-12-01 L30848A	1.06	2.94	0.03	10.42	8.37	0.0080	0.0461	0.00	0.44
28/05/2013	FRO-TCR-12-01 L30848AR	0.83	2.89	0.03	8.35	8.34	0.0073	0.0458	0.00	0.44
28/05/2013	FRO-TCR-12-01 L30862A	0.65	6.09	0.02	7.45	19.42	0.0057	0.0311	0.00	0.07

28/05/2013	FRO-TCR-12-01 L30862AR	0.67	6.10	0.03	7.74	19.28	0.0026	0.0325	0.00	0.07
28/05/2013	FRO-TCR-12-01 L30876A	0.91	2.14	0.04	10.80	10.48	0.0085	0.0787	0.00	0.21
28/05/2013	FRO-TCR-12-01 L30876AR	0.99	2.15	0.04	11.43	10.50	0.0040	0.0785		0.20
10/06/2013	FRO-TCR-12-02 L30815A	1.19	4.25	0.03	19.12	13.14	0.0020	0.0304		0.13
10/06/2013	FRO-TCR-12-02 L30815AR	1.20	4.31	0.02	18.85	13.14	0.0024	0.0290		0.13
10/06/2013	FRO-TCR-12-02 L30829A	0.60	1.82	0.03	7.65	9.01	0.0038	0.0640		0.42
10/06/2013	FRO-TCR-12-02 L30829AR	0.68	1.88	0.03	8.38	9.24	0.0041	0.0647	0.00	0.41
10/06/2013	#10473	1.80	94.27	0.03	2.23	172.59	0.0101	0.2181	0.00	0.01
10/06/2013	#10473R	1.75	96.77	0.03	2.26	176.65	0.0122	0.2093	0.00	0.01
10/06/2013	#10477	1.77	98.35	0.02	2.16	175.12	0.0099	0.2114	0.00	0.02
10/06/2013	#10477R	1.94	99.69	0.02	2.33	177.24	0.0103	0.2105	0.00	0.02
26/06/2013	FRO-TCR-12-02b L30934A	2.00	1.65	0.04	4.03	8.58	0.0014	0.0184		0.22
26/06/2013	FRO-TCR-12-02b L30934AR	2.16	1.61	0.03	4.28	8.50		0.0171		0.21
23/07/2013	#10499	1.95	39.54	0.03	0.93	103.29	0.0050	0.0991	0.00	0.04
23/07/2013	#10499R	2.04	39.79	0.03	0.96	104.80	0.0054	0.1073	0.00	0.04
23/07/2013	#10513	6.54	33.47	0.04	1.81	166.24	0.0017	0.0351	0.00	0.12
23/07/2013	#10513R	6.51	32.84	0.04	1.80	163.50	0.0019	0.0354	0.00	0.12
23/07/2013	#10527	2.49	27.04	0.03	0.66	102.55		0.0024	0.00	0.29
23/07/2013	#10527R	2.49	26.92	0.03	0.66	99.98	0.0003	0.0023	0.00	0.29
23/07/2013	#10542	1.82	31.44	0.04	0.77	113.59	0.0021	0.0466		0.21
23/07/2013	#10542R	1.86	31.58	0.04	0.80	113.65	0.0033	0.0470		0.21
23/07/2013	#10558	191.76	3.52	0.05		7.47	0.0019	0.0057		0.54
23/07/2013	#10558R	188.95	3.61	0.05		7.71	0.0021	0.0053		0.54
23/07/2013	EV-BRO-12-01 L30457A	1.93	7.09	0.04	5.15	13.51	0.0016	0.0164	0.00	0.13
23/07/2013	EV-BRO-12-01 L30457AR	1.84	7.03	0.04	5.08	13.60	0.0014	0.0182	0.00	0.13
08/08/2013	EV-BRD-12-01 L30471A	0.65	11.17	0.07	7.05	20.59	0.0025	0.0279	0.00	0.10
08/08/2013	EV-BRD-12-01 L30471AR	0.70	11.27	0.07	7.32	20.50	0.0026	0.0298	0.00	0.10
08/08/2013	EV-BRD-12-01 L30479A	0.59	12.52	0.07	7.41	19.66	0.0024	0.0236	0.00	0.08
08/08/2013	EV-BRD-12-01 L30479AR	0.59	12.04	0.05	7.03	19.43	0.0015	0.0261	0.00	0.09
08/08/2013	EV-BRD-12-01 L30486A	0.78	22.28	0.10	7.35	45.62	0.0022	0.0239	0.00	0.07
08/08/2013	EV-BRD-12-01 L30486AR	0.77	22.25	0.10	7.38	45.54	0.0017	0.0228	0.00	0.07

08/08/2013	EV-BRD-12-01 L30500A	2.30	25.16	0.03	16.28	39.34	0.0039	0.0445	0.00	0.06
08/08/2013	EV-BRD-12-01 L30500AR	2.38	25.67	0.02	16.93	39.27	0.0035	0.0451	0.00	0.06
08/08/2013	EV-BRD-12-01 L30514A	1.15	23.62	0.05	8.53	55.37	0.0057	0.0771	0.00	0.04
08/08/2013	EV-BRD-12-01 L30514AR	1.10	23.48	0.04	8.21	53.93	0.0053	0.0796	0.00	0.04
08/08/2013	EV-BRD-12-01 L30529A	1.37	4.06	0.03	22.33	13.50	0.0036	0.0504		0.31
08/08/2013	EV-BRD-12-01 L30529AR	1.38	4.03	0.03	22.40	13.15	0.0040	0.0517		0.31
08/08/2013	EV-BRD-12-01 L30543A	1.28	5.94	0.05	21.00	17.70	0.0032	0.0365	0.00	0.16
08/08/2013	EV-BRD-12-01 L30543AR	1.26	5.94	0.05	20.31	17.60	0.0037	0.0375	0.00	0.16
08/08/2013	EV-BRD-12-02b L30557A	0.79	12.00	0.04	6.32	23.65	0.0023	0.0355	0.00	0.07
08/08/2013	EV-BRD-12-02b L30557AR	0.82	11.92	0.04	6.42	23.59	0.0030	0.0382	0.00	0.07
14/08/2013	EV-BRD-12-02b L30583A	1.70	8.54	0.04	13.59	20.63	0.0020	0.0315	0.00	0.09
14/08/2013	EV-BRD-12-02b L30583AR	1.62	8.32	0.04	13.38	20.48	0.0020	0.0318	0.00	0.09
14/08/2013	FRO-TCR-DL1 L01026	0.90	9.81	0.05	8.46	34.22	0.0051	0.0760		0.07
14/08/2013	FRO-TCR-DL1 L01026R	0.97	9.82	0.04	8.94	33.80	0.0057	0.0794		0.07
14/08/2013	FRO-TCR-DL2 L01051-1	2.24	3.36	0.08	7.42	13.23	0.0028	0.0428	0.00	0.18
14/08/2013	FRO-TCR-DL2 L01051-1R	2.34	3.50	0.08	7.74	13.48	0.0024	0.0435	0.00	0.17
14/08/2013	FRO-TCR-DL2 L01054-2	1.50	11.14	0.05	6.36	38.36	0.0054	0.0900	0.00	0.06
14/08/2013	FRO-TCR-DL2 L01054-2R	1.49	11.36	0.05	6.19	38.46	0.0051	0.0903	0.00	0.06
14/08/2013	FRO-TCR-DL2 L01058-3	2.30	3.39	0.04	8.91	11.27	0.0024	0.0362		0.10
14/08/2013	FRO-TCR-DL2 L01058-3R	2.28	3.46	0.04	8.81	11.25	0.0029	0.0375		0.10
14/08/2013	#10572	4.78	257.79	0.07	5.60	462.29	0.0277	0.5491	0.00	0.03
14/08/2013	#10572R	4.28	252.80	0.07	5.16	461.12	0.0320	0.5594	0.00	0.03
14/08/2013	#10586	1.05	40.82	0.07	0.83	117.25	0.0051	0.0949		0.05
14/08/2013	#10586R	1.05	40.16	0.07	0.86	117.81	0.0056	0.0932	0.00	0.06
25/01/2013	30281A1	17.05	50.57	0.03	8.07	164.30	0.0008	0.0089	0.00	0.17
25/01/2013	30281A1R	18.69	52.94	0.04	8.95	168.69	0.0008	0.0094	0.00	0.17
25/01/2013	30323A	77.52	94.61	0.13	21.63	123.37	0.0044	0.0240		0.39
25/01/2013	30323AR	78.37	90.20	0.14	21.97	122.37	0.0029	0.0227	0.00	0.39
25/01/2013	30294A	40.54	142.84	0.12	37.80	376.19	0.0032	0.0752	0.00	0.88
25/01/2013	30294AR	40.70	143.89	0.12	38.84	372.41	0.0047	0.0918	0.00	0.87
25/01/2013	30322A	80.57	69.89	0.05	25.90	119.28	0.0019	0.0086		0.41

25/01/2013	30322AR	87.19	67.80	0.05	27.27	117.91	0.0015	0.0119		0.41
05/09/2013	# 10604	1.37	34.93	0.03	0.85	113.74	0.0039	0.0710		0.17
05/09/2013	# 10604R	1.39	36.01	0.03	0.85	116.21	0.0051	0.0711		0.17
05/09/2013	# 10618	5.23	303.62	0.05	6.00	490.13	0.0429	0.5992	0.00	0.03
05/09/2013	# 10618R	5.07	301.64	0.04	5.76	486.78	0.0495	0.5975	0.00	0.03
05/09/2013	# 10632	2.45	21.03	0.07	0.79	69.88	0.0005	0.0050	0.00	0.09
05/09/2013	# 10632R	2.60	20.98	0.07	0.81	69.99	0.0006	0.0059	0.00	0.09
05/09/2013	CRO-CC3-12-01 L30706A	3.02	7.96	0.05	8.38	35.60	0.0080	0.0759		0.10
05/09/2013	CRO-CC3-12-01 L30706AR	3.03	7.97	0.04	8.37	35.75	0.0078	0.0803	0.00	0.09
04/10/2013	#10677	8.54	32.64	0.01	0.93	112.38	0.0016	0.0531	0.00	0.08
04/10/2013	#10677R	8.55	27.76	0.02	0.92	111.33	0.0019	0.0532	0.00	0.08
30/10/2013	LC-WLC-12-02b L11157A	21.52	59.46	0.04	2.69	147.30	0.0022	0.0384	0.00	0.03
30/10/2013	LC-WLC-12-02b L11157AR	21.19	59.73	0.04	2.64	144.03	0.0016	0.0409	0.00	0.03
30/10/2013	LC-WLC-12-02b L10691A	4.98	281.30	0.06	4.89	451.06	0.0344	0.6252	0.00	0.04
30/10/2013	LC-WLC-12-02b L10691AR	5.13	281.50	0.06	5.03	457.33	0.0320	0.6184	0.00	0.04
17/06/2013	# 10484	1.12	78.82	0.02	2.06	151.43	0.0081	0.1540	0.00	0.01
17/06/2013	# 10484R	1.16	78.55	0.02	2.11	151.47	0.0078	0.1547	0.00	0.01

Blind Duplicates										
Date	**Sample ID**	**Na**	**Mg**	**P**	**K**	**Ca**	**As**	**Se**	**Cd**	**Ba**
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
10/10/2013	Oct10/13,L30413A	0.53	8.43	0.06	5.57	19.48	0.0010	0.0107	0.0000	0.0892
10/10/2013	LC-WLC-12-02a L30413A	0.47	7.21	0.06	5.32	16.72	0.0040	0.0120	0.0000	0.0951
24/10/2013	Oct24/13	0.98	8.55	0.02	7.86	18.61	0.0018	0.0322	0.0000	0.0647
24/10/2013	LC-WLC-12-02b L30451A	0.97	7.65	0.04	7.66	16.24	0.0025	0.0352	0.0000	0.0673
01/10/2013	Oct 1/13 L30355A	1.14	6.12	0.03	12.59	17.74	0.0008	0.0099	0.0000	0.1435
01/10/2013	L30355A	0.94	5.44	0.05	12.56	15.22	0.0009	0.0121		0.1465
30/09/2013	Sep30/13	0.33	6.46	0.05	1.37	12.46	0.0005	0.0087	0.0001	0.0358
30/09/2013	LC-WLC-12-02a L30348A	0.32	5.96	0.06	1.27	11.87	0.0001	0.0100	0.0001	0.0363
05/09/2013	Sep5/13	0.64	37.21	0.02	7.62	134.10	0.0036	0.0400	0.0004	0.0228
05/09/2013	L30779A GHO-CCR-12-01	0.54	34.46	0.05	6.51	120.30	0.0048	0.0456	0.0004	0.0215
21/08/2013	Aug 21/13	0.39	13.93	0.02	3.51	51.36	0.0010	0.0122	0.0002	0.0340
21/08/2013	GHO-CCR-12-01 L30754A	0.37	13.19	0.03	3.24	48.37	0.0011	0.0137	0.0002	0.0345
13/08/2013	Aug 13/13	15.48	17.14	0.02	6.54	63.27	0.0034	0.0481	0.0000	0.0568
13/08/2013	CRO-CC3-12-01 L30691A	14.89	16.75	0.05	5.77	56.99	0.0040	0.0525		0.0563
26/08/2013	Aug 26/13R	0.31	5.64	*0.00*	3.12	22.51	0.0011	0.0170	0.0002	0.1630
26/08/2013	GHO-CCR-12-01 L30760A	0.31	5.39	0.03	2.63	17.86	0.0007	0.0109	0.0001	0.1155
27/08/2013	Aug 27/13	0.66	17.52	*0.00*	4.22	85.40	0.0021	0.0388	0.0001	0.0350
27/08/2013	GHO-CCR-12-01 L30766A	0.62	17.06	0.03	3.59	75.23	0.0022	0.0254	0.0001	0.0285
08/10/2013	Oct8/13	0.66	6.87	0.02	6.10	14.92	0.0022	0.0244	0.0000	0.0709
08/10/2013	LC-WLC-12-02a L30448A	0.72	6.26	0.04	5.93	13.68	0.0031	0.0251	0.0000	0.0699
18/07/2013	Jul15/13	1.09	30.79	0.02	9.45	43.11	0.01	0.08	0.00	0.04
18/07/2013	EV-BRD-12-01 L30508A	0.99	27.66	0.03	8.36	38.63	0.01	0.09	0.00	0.04
18/07/2013	Jul16/13	0.73	7.40	0.02	11.21	19.30	0.01	0.07	0.00	0.12
18/07/2013	EV-BRD-12-01 L30528A	0.64	6.48	0.03	9.45	17.54	0.00	0.08	0.00	0.12
18/07/2013	Jul17/13	1.42	9.95	0.02	18.24	35.34	0.00	0.06		0.08
18/07/2013	EV-BRD-12-01 L30544A	1.35	9.89	0.06	15.79	32.98	0.00	0.06	0.00	0.08
25/07/2013	Jul21/13	1.21	18.34	0.02	9.38	55.78	0.00	0.04	0.00	0.04
25/07/2013	EV-BRD-12-02b L30571A	1.10	18.64	0.05	7.84	49.48	0.00	0.04	0.00	0.04

25/07/2013	Jul22/13	1.00	12.86	0.02	7.55	32.06	0.00	0.02	0.00	0.05
25/07/2013	EV-BRD-12-02b L30581A	0.99	12.95	0.03	6.82	28.25	0.00	0.03	0.00	0.05
25/07/2013	Jul23/13	1.21	19.00	0.02	9.68	55.96	0.01	0.12	0.00	0.06
25/07/2013	FRO-TCR-DL1 L01024	1.23	19.88	0.05	8.54	50.76	0.01	0.13	0.00	0.06
26/07/2013	Jul24/13	2.72	4.38	0.02	9.65	18.25	0.00	0.04		0.17
26/07/2013	FRO-TCR-DL2 L01051-2	2.33	4.31	0.06	8.53	15.24	0.00	0.05	0.00	0.18
26/07/2013	Jul26/13	1.23	12.73	0.02	9.82	42.95	0.00	0.06	0.00	0.08
26/07/2013	FRO-TCR-DL2 L01063	1.16	12.47	0.05	8.53	39.29	0.00	0.07	0.00	0.08
20/11/2013	Nov 18/13 BD	65.09	2.11	0.02	2.06	6.95	0.00	0.01		0.11
20/11/2013	CRO-B5-12-01 L30647A	62.45	2.08	0.09	1.75	6.36	0.00	0.01		0.12
20/11/2013	Nov 20/13 BD	63.99	1.35	0.02	1.17	3.40	0.00	0.01		0.12
20/11/2013	CRO-B5-12-01 L30652A	65.08	1.26	0.05	0.00	3.43	0.00	0.01		0.12
26/11/2013	Nov 21/13 BD	46.68	10.92	0.01	0.00	32.47	0.00	0.01	0.00	0.05
26/11/2013	CRO-B5-12-01 L30655A	47.30	11.41	0.08	0.00	33.68	0.00	0.01	0.00	0.08
26/09/2013	Sep 23/13 BD	91.50	0.38	0.02	0.00	1.07	0.00	0.04	0.00	0.11
26/09/2013	CRO-B5-12-01 L30635A	102.13	0.35	0.04	0.00	1.00	0.00	0.04	0.00	0.08
26/11/2013	Nov 25/13 BD	53.96	10.75	0.01	5.67	49.64	0.00	0.01	0.00	0.04
26/11/2013	CRO-B5-12-01 L30661A	54.94	10.35	0.02	5.78	43.79	0.00	0.01	0.00	0.05
05/12/2013	Nov 27/13 BD	71.10	1.28	0.02	0.92	3.79	0.00	0.02	0.00	0.07
05/12/2013	CRO-B5-12-01 L30667A	74.82	1.31	0.04	1.26	3.82	0.00	0.02	0.00	0.08
18/12/2013	Dec 10/13 BD	34.19	14.90	0.01	4.25	50.03	0.00	0.03	0.00	0.05
18/12/2013	CRO-B5-12-01 L30680A	35.32	13.58	0.04	4.46	43.39	0.00	0.03	0.00	0.06

Calibration Control Standard										
		Na	**Mg**	**P**	**K**	**Ca**	**As**	**Se**	**Cd**	**Ba**
	CS							0.0098		
26/02/2013	Se 9.79 ppb, SPC							0.0096		
04/04/2013	Se, 9.79ppb							0.0091		
14/03/2013	Se4-spc-9.79ppb							0.0107		
20/03/2013	Se4-spc-9.79ppb							0.0090		
	CS							0.0021		
04/04/2013	Se, 2.05ppb							0.0022		
14/03/2013	Se5-spc-2.05ppb							0.0022		
20/03/2013	Se5-spc-2.05ppb							0.0019		
20/03/2013	Se5-spc-2.05ppb							0.0021		
	CS							0.2142		
26/02/2013	Se2-spc-214.2ppb							0.2067		
14/03/2013	Se2-spc-214.2ppb							0.2292		
20/03/2013	Se2-spc-214.2ppb							0.2140		
	CS							0.0458		
26/02/2013	Se, 45.8ppb							0.0450		
04/04/2013	Se, 45.8ppb							0.0409		
14/03/2013	Se3-spc-45.8ppb							0.0488		
20/03/2013	Se3-spc-45.8ppb							0.0466		
	CS						0.00521	0.0052	0.00518	
17/06/2013	As5.21-Se5.16-Cd5.18ppb						0.0049	0.0051	0.0049	
10/06/2013	As5.21-Se5.16-Cd5.18ppb						0.0055	0.0055	0.00	
10/06/2013	As5.21-Se5.16-Cd5.18ppb						0.0051	0.0047	0.00	
10/06/2013	As5.21-Se5.16-Cd5.18ppb						0.0048	0.0051	0.00	
	CS						0.00521	0.0052	0.0052	
26/06/2013	As5.214Se5.158Cd5.178ppb						0.0048		0.0048	
26/06/2013	As5.214Se5.158Cd5.178ppb						0.0056		0.0055	
26/06/2013	As5.214Se5.158Cd5.178ppb						0.0054		0.0054	
26/06/2013	As5.214Se5.158Cd5.178ppb						0.0047		0.0047	

26/06/2013	As5.214Se5.158Cd5.178ppb						0.0049		0.0046	
26/06/2013	As5.214Se5.158Cd5.178ppb						0.0046		0.0047	
	CS						0.0066	0.0065	0.0066	
14/08/2013	As6.608Se6.537Cd6.562						0.0061	0.0060	0.0059	
14/08/2013	As6.608Se6.537Cd6.562						0.0060	0.0059	0.0059	
14/08/2013	As6.608Se6.537Cd6.562						0.0063	0.0065	0.0060	
14/08/2013	As6.608Se6.537Cd6.562						0.0058	0.0062	0.0060	
14/08/2013	As6.608Se6.537Cd6.562						0.0059	0.0059	0.0061	
26/06/2013	As6.608Se6.537Cd6.562ppb						0.0061	0.0071	0.0059	
26/06/2013	As6.608Se6.537Cd6.562ppb						0.0060	0.0064	0.0060	
26/06/2013	As6.608Se6.537Cd6.562ppb						0.0059	0.0064	0.0060	
26/06/2013	As6.608Se6.537Cd6.562ppb						0.0060	0.0064	0.0061	
26/06/2013	As6.608Se6.537Cd6.562ppb						0.0059	ud	0.0059	
	CS						0.0066	0.0066	0.0066	
05/09/2013	As6.647Se6.576Cd6.601						0.0064	0.0060	0.01	
05/09/2013	As6.647Se6.576Cd6.601						0.0063	0.0060	0.01	
05/09/2013	As6.647Se6.576Cd6.601						0.0065	0.0063	0.01	
	CS							0.0020		
12/02/2013	Se2.0166 ppb							0.0022		
12/02/2013	Se2.0166 ppb							0.0015		
12/02/2013	Se2.0166 ppb							0.0019		
12/02/2013	Se2.0166 ppb							0.0024		
12/02/2013	Se2.0166 ppb							0.0022		
12/02/2013	Se2.0166 ppb							0.0021		
	CS	23400	21600	1527.4	14900	50900	0.6500	0.0880	0.13	683
03/04/2013	BCR-2	23182.29	21370.26	1607.89	16603.30	49165.39			0.58	646.26
24/07/2013	BCR-2	24178.72	21509.14	1688.43	15390.87	57327.10				688.14
24/07/2013	BCR-2	26869.42	19987.59	1630.09	16513.64	54432.07				686.58
24/07/2013	BCR-2	22972.61	20460.84	1574.01	14948.96	54708.58				671.88
24/07/2013	BCR-2	23833.98	21297.86	1541.17	15503.38	63439.32				669.58
24/07/2013	BCR-2	23459.56	20794.58	1602.60	14695.20	55393.58				672.21

24/07/2013	BCR-2	23988.38	20296.69	1564.49	15104.76	47311.75				696.27
24/07/2013	BCR-2	23176.27	20619.63	1575.99	15154.40	52606.51				674.23
14/03/2013	BCR-2	22939.12	19568.91	1591.19	15861.20	52163.32				695.19
14/03/2013	BCR-2	22990.56	19958.62	1593.38	15293.50	51073.40			0.22	680.65
14/03/2013	BCR-2	24495.23	19634.06	1607.33	15474.19	53162.67			0.24	691.09
14/03/2013	BCR-2	24038.99	19246.50	1590.12	15848.30	50394.96			0.27	695.20
14/03/2013	BCR-2	23968.85	19061.31	1618.92	15444.64	47873.32			0.29	692.42
14/03/2013	BCR-2	22498.47	19357.95	1613.60	16310.00	50017.16			0.01	690.94
14/03/2013	BCR-2	23955.82	19049.70	1617.35	15438.24	47800.08			0.17	692.39
14/03/2013	BCR-2	22535.06	19396.11	1621.26	16370.41	50080.48				691.09
14/03/2013	BCR-2	25635.78	20140.12	1638.89	17057.22	52048.75			0.31	696.12
26/02/2013	BCR-2	23799.60	21514.61	1545.13	14312.90	47404.91	0.6974		0.13	655.78
26/02/2013	BCR-2	24177.06	21243.51	1499.83	14644.04	47565.22	1.6764		0.08	661.19
26/02/2013	BCR-2	24854.67	21774.41	1512.52	15112.92	49933.75	2.8514			672.02
12/02/2013	BCR-2	23631.22	19308.95	1578.82	14831.78	51133.26			0.30	678.69
12/02/2013	BCR-2	23856.62	20015.88	1590.59	15301.46	49559.38			0.08	666.03
12/02/2013	BCR-2	23940.32	20168.68	1609.76	15098.05	48972.59			0.07	665.46
12/02/2013	BCR-2	23174.45	20337.87	1605.41	15325.90	50938.06			0.20	672.29
12/02/2013	BCR-2	24234.47	20644.95	1623.51	16279.77	53715.42			0.06	678.12
12/02/2013	BCR-2	24064.53	19394.80	1558.82	17482.09	54662.45			0.07	687.43
12/02/2013	BCR-2	23022.71	19606.42	1611.24	16795.24	51045.45			0.01	664.53
12/02/2013	BCR-2	23934.75	19532.84	1617.41	17751.96	51516.37			0.16	665.55
20/02/2013	BCR-2	25263.88	22854.66	1568.27	15527.57	49438.60				671.13
20/02/2013	BCR-2	24522.53	22344.58	1576.73	15251.43	49988.62				669.82
20/02/2013	BCR-2	23728.28	21832.15	1582.46	16009.72	51837.07				673.61
02/05/2013	BCR-2	20093.87	20167.49	1559.22	14488.35	48155.51			0.63	619.01
02/05/2013	BCR-2	22130.99	21158.29	1632.61	15682.54	49862.62			0.69	635.39
02/05/2013	BCR-2	22330.25	21328.94	1626.95	15780.52	50834.62			0.77	631.40
02/05/2013	BCR-2	24825.70	20904.62	1564.13	16801.00	50274.25			0.88	612.61
22/05/2013	BCR-2	21632.98	20682.78	1572.53	15515.48	48628.41				628.73
10/06/2013	BCR-2	22725.52	20675.83	1602.70	16217.56	48056.86	2.0701		0.27	609.98

10/06/2013	BCR-2	22571.25	20049.99	1655.60	15997.32	46461.49	1.4756		0.14	614.59
26/06/2013	BCR-2	25007.20	21117.58	1670.67	15724.21	51759.55	2.1638		0.08	655.98
26/06/2013	BCR-2	23560.69	20905.73	1674.78	15495.12	50896.38	0.0481		0.01	674.02
26/06/2013	BCR-2	25017.17	21027.20	1661.00	15952.67	49652.90	2.0501		0.12	666.37
23/07/2013	BCR-2	24685.04	20685.59	1670.91	16040.84	53311.71	2.6648			643.08
23/07/2013	BCR-2	24711.84	21082.95	1674.63	16019.33	50836.62	4.3168		0.10	641.82
08/08/2013	BCR-2	21435.63	20288.06	1606.18	15192.91	47640.90	3.9973		0.94	639.15
08/08/2013	BCR-2	23078.67	19934.18	1515.02	15894.05	47023.34	2.0809		1.02	644.50
14/08/2013	BCR-2	22285.10	19532.65	1570.92	14978.63	46993.82			0.45	646.11
14/08/2013	BCR-2	24241.55	19337.44	1562.91	15564.56	47733.25			0.37	633.77
25/01/2013	BCR-2	21121.78	19812.51	1604.95	15570.66	51213.89			0.07	672.96
25/01/2013	BCR-2	22063.40	19953.25	1605.48	16048.33	50723.56			0.17	677.85
05/09/2013	BCR-2	21931.06	18706.22	1585.70	15265.82	47490.30	1.3552			642.06
05/09/2013	BCR-2	22884.91	19174.42	1600.22	15936.35	47420.19	0.2081		0.06	636.58
04/10/2013	BCR-2	21509.47	21044.61	1477.72	15070.48	47592.86			0.14	625.77
04/10/2013	BCR-2	24426.98	16494.16	1676.99	16963.03	50355.49			0.15	632.12
30/10/2013	BCR-2	24256.99	20298.36	1544.30	15280.27	47766.46	0.2488			615.12
30/10/2013	BCR-2	24790.37	20538.51	1516.30	15304.51	47156.79	2.4219		0.07	627.08
30/10/2013	BCR-2	24049.48	20464.39	1564.89	14578.60	47192.72	1.7211		0.01	613.94
17/06/2013	BCR-2	24916.23	20373.35	1681.64	15699.83	52158.91			0.15	663.61
	CS	2.4	1.6	0	0.68	6.2	0.0007	0.0000	0.000012	0.0122
03/04/2013	SLRS-4	1.96	1.53	0.01	0.62	5.03	0.0006	ud	0.00	0.01
24/07/2013	SLRS-4	2.44	1.47	0.01	0.64	6.08	0.0008	ud	0.00	0.01
24/07/2013	SLRS-4	2.43	1.45	0.01	0.63	6.00	0.0009	ud	0.00	0.01
02/05/2013	SLRS-4	2.35	1.47	0.00	0.66	5.53	0.0007	0.0002	0.00	0.01
02/05/2013	SLRS-4	2.47	1.48	0.01	0.68	5.53	0.0008	0.0002	0.00	0.01
22/05/2013	SLRS-4	2.79	1.48	0.01	0.68	5.50	0.0007	ud	0.00	0.01
22/05/2013	SLRS-4	2.44	1.45	0.01	0.63	5.35	0.0007	ud	0.00	0.01
22/05/2013	SLRS-4	2.65	1.49	0.01	0.68	5.43	0.0006	ud	0.00	0.01
28/05/2013	SLRS-4	2.83	1.46	0.01	0.66	5.78	0.0008	0.0002	0.00	0.01
28/05/2013	SLRS-4	2.77	1.46	0.01	0.65	5.63	0.0008	0.0003	0.00	0.01

23/07/2013	SLRS-4	2.49	1.39	0.00	0.67	5.33	0.0007	ud	0.00	0.01
23/07/2013	SLRS-4	2.43	1.46	0.00	0.65	5.35	0.0007	ud	0.00	0.01
23/07/2013	SLRS-4	2.40	1.46	0.00	0.66	5.39	0.0008	ud	0.00	0.01
25/01/2013	SLRS-4	2.44	1.43	0.01	0.67	5.67	0.0008	ud	0.00	0.01
25/01/2013	SLRS-4	2.60	1.46	0.01	0.71	5.82	0.0009	ud	0.00	0.01
25/01/2013	SLRS-4	2.64	1.49	0.01	0.74	5.84	0.0007	ud	0.00	0.01
05/09/2013	SLRS-4	2.32	1.45	0.00	0.66	5.89	0.0006	0.0002	ud	0.01
05/09/2013	SLRS-4	2.29	1.39	0.00	0.63	5.68	0.0007	0.0002	0.00	0.01
05/09/2013	SLRS-4	2.34	1.44	0.00	0.64	5.68	0.0007	0.0002	ud	0.01
17/06/2013	SLRS-4-145	2.67	1.47	0.00	0.70	5.57	0.0008	ud	0.00	0.01
10/06/2013	SLRS-4-145	2.34	1.45	0.00	0.62	6.13	0.0009	ud	0.00	0.01
	CS	20.23	7.841	0	1.984	31.5	0.0590	0.0117	0.00641	0.531
14/03/2013	SRM 1643e-3	26.08	8.86	0.04	1.75	37.23	0.0481	0.0089	0.00	0.53
14/03/2013	SRM 1643e-3	24.55	8.65	0.04	1.73	32.91	0.0465	0.0086	0.00	0.52
14/03/2013	SRM 1643e-3	24.88	8.44	0.03	1.69	31.91	0.0470	0.0089	0.00	0.52
14/03/2013	SRM 1643e-3	24.26	8.68	0.04	1.65	32.11	0.0473	0.0089	0.00	0.53
14/03/2013	SRM 1643e-3	26.10	8.97	0.03	1.68	32.43	0.0472	0.0094	0.00	0.53
14/03/2013	SRM 1643e-3	25.31	9.04	0.04	1.65	35.71	0.0470	0.0092	0.00	0.53
14/03/2013	SRM 1643e-3	26.38	9.21	0.03	1.74	36.18	0.0470	0.0095	0.00	0.52
02/05/2013	SRM 1643e	21.81	8.38	0.01	1.75	27.59	0.0440	0.0094	0.00	0.50
02/05/2013	SRM 1643e	23.59	8.13	0.01	1.80	26.12	0.0407	0.0084	0.00	0.48
20/03/2013	SRM1643e	20.36	7.77	0.03	1.29	27.14	0.0380	0.0072	0.00	0.50
01/06/2013	SRM1643e-133	19.77	7.59	0.03	1.59	30.94	0.0406	0.0091	0.01	0.48
01/06/2013	SRM1643e-133	20.75	7.75	0.03	1.71	31.17	0.0403	0.0090	0.01	0.48
01/06/2013	SRM1643e-133	20.89	7.86	0.03	1.73	31.83	0.0422	0.0088	0.00	0.50
	CS	0.47	10.47	0.02	0.27	20.44	0.0011	0.0201	0.0001	0.01
14/03/2013	SRW1-5	0.39	8.71	0.05	0.26	20.27	0.0017	0.0213	0.00	0.01
20/02/2013	SRW1x5	0.48	11.18	0.04	0.24	18.00	0.0009	0.0214	0.00	0.01
12/02/2013	SRW1-5-1	0.49	10.50	0.02	0.26	21.76	0.0009	0.0197	0.00	0.01
12/02/2013	SRW1-5-1	0.48	10.45	0.02	0.26	22.36	0.0011	0.0191	0.00	0.01
12/02/2013	SRW1-5-1	0.48	10.34	0.02	0.25	22.15	0.0009	0.0203	0.00	0.01

12/02/2013	SRW1-5-1	0.49	10.42	0.02	0.26	22.01	0.0008	0.0196	0.00	0.01
02/05/2013	SRW1-5-1	0.44	10.57	0.00	0.26	18.71	0.0006	0.0190	0.00	0.01
02/05/2013	SRW1-5-1	0.44	10.44	0.00	0.27	18.46	0.0010	0.0194	0.00	0.01
20/03/2013	SRW1x5	0.46	9.70	0.01	0.25	18.73	0.0012	0.0189	0.00	0.01
22/05/2013	SRW1-5-1	0.49	11.27	0.01	0.28	20.39	0.0009	0.0188	0.00	0.01
22/05/2013	SRW1-5-1	0.46	11.17	0.01	0.26	19.63	0.0011	0.0195	0.00	0.01
22/05/2013	SRW1-5-1	0.48	11.25	0.01	0.27	20.48	0.0009	0.0200	0.00	0.01
01/06/2013	SRW1-5-1	0.48	9.62	0.01	0.28	19.20	0.0029	0.0198	0.00	0.01
01/06/2013	SRW1-5-1	0.47	10.07	0.01	0.29	20.01	0.0016	0.0202	0.00	0.01
01/06/2013	SRW1-5-1	0.52	9.93	0.01	0.32	19.68	0.0021	0.0197	0.00	0.01
28/05/2013	SRW1-5-1	0.47	11.73	0.01	0.26	20.30	0.0010	0.0198	0.00	0.01
28/05/2013	SRW1-5-1	0.46	11.91	0.01	0.26	20.16	0.0012	0.0202	0.00	0.01
28/05/2013	SRW1-5-1	0.51	12.06	0.01	0.28	20.50	0.0011	0.0201	0.00	0.01
23/07/2013	SRW1-5-1	0.48	10.16	0.02	0.27	20.55	0.0011	0.0196	0.00	0.01
23/07/2013	SRW1-5-1	0.49	10.16	0.02	0.26	20.88	0.0012	0.0202	0.00	0.01
23/07/2013	SRW1-5-1	0.46	10.18	0.02	0.25	20.34	0.0009	0.0205	0.00	0.01
08/08/2013	SRW1-5-1	0.55	9.33	0.03	0.77	17.95	0.0022	0.0215	0.00	0.01
08/08/2013	SRW1-5-1	0.75	10.35	0.03	0.68	18.46	0.0023	0.0208	0.00	0.01
08/08/2013	SRW1-5-1	0.48	10.57	0.01	0.26	20.27	0.0014	0.0197	0.00	0.01
08/08/2013	SRW1-5-1	0.52	10.70	0.01	0.28	20.61	0.0016	0.0201	0.00	0.01
08/08/2013	SRW1-5-1	0.55	9.33	0.03	0.77	17.95	0.0022	0.0183	0.00	0.01
08/08/2013	SRW1-5-1	0.75	10.35	0.03	0.68	18.46	0.0023	0.0167	0.00	0.01
14/08/2013	SRW1-5-1	0.50	10.39	0.01	0.28	19.98	0.0012	0.0201	0.00	0.01
14/08/2013	SRW1-5-1	0.48	10.18	0.01	0.27	20.34	0.0014	0.0202	0.00	0.01
14/08/2013	SRW1-5-1	0.45	10.18	0.01	0.26	20.14	0.0011	0.0192	0.00	0.01
14/08/2013	SRW1-5-1	0.44	11.05	0.01	0.28	21.10	0.0013	0.0218	0.00	0.01
14/08/2013	SRW1-5-1	0.46	11.38	0.01	0.29	21.06	0.0012	0.0218	0.00	0.01
14/08/2013	SRW1-5-1	0.46	11.51	0.01	0.29	20.85	0.0012	0.0221	0.00	0.01
04/10/2013	SRW1-5	0.48	9.46	0.00	0.27	19.39	0.0009	0.0195	0.00	0.01
04/10/2013	SRW1-5	0.51	7.47	0.00	0.29	19.88	0.0010	0.0201	0.00	0.01